University of Alberta

Phosphorus Removal from Raw Sewage Using Waste Alum Sludge

By

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ABSTRACT

Co-disposal of water treatment plant (WTP) alum sludge with wastewater treatment plant (WWTP) sludge has been adopted in a number of communities where suitable methods exist to convey the WTP sludge and adequate solids handling capacity exists at the WWTP. In this study, phosphorus removal efficiency of WTP alum sludge from raw wastewater was evaluated. The results of this study confirmed that alum sludge had a good phosphorus adsorption capacity. The Freundlich isotherm parameters, K and 1/n, did not reveal a consistent response to changes in temperature (5 to 19°C), but overall the adsorption density (K) tended to increase with decreasing temperature. No significant effect of pH was observed for orthophosphate removal. In contrast, adsorption of total phos

phorus tended to increase with increasing pH (pH 6.5 to 8). Desorption testing indicated less mobility for previously adsorbed orthophosphate and total phosphorus and no significant difference between the mass of phosphorus desorbed at pH 5 and 9.

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DEDICATION

To my parents, for their

undying love, sacrifice and moral support

TABLE OF CONTENTS

1 INTRODUCTION 1

1.1 Hypothesis 2

1.2 Objectives 3

1.3 Outline of the thesis 3

2 LITERATURE REVIEW 4

2.1 Phosphorus in Wastewater 4

2.1.1 Environmental significance 6

2.1.2 Phosphorus discharge limit 7

2.2 Methods of phosphorus removal 7

2.2.1 Phosphorus removal by chemical precipitation 7

2.2.2 Phosphorus removal by adsorption 8

2.2.3 Phosphorus removal by biological processes 12

2.3 Waste alum sludge: generation, handling and disposal 13

2.3.1 Sludge treatment 13

2.3.2 Disposal 22

2.4 Wastewater treatment solids: generation, handling and disposal 26

2.4.1 Sludge treatment 26

2.4.2 Disposal 36

2.4.3 Bio-solids handling and disposal in the Gold Bar wastewater treatment plant 38

2.5 Use of alum sludge for phosphorus removal from municipal wastewater 39

2.6 Effect of temperature and pH on phosphorus removal 42

2.6.1 Effect of temperature 42

2.6.2 Effect of pH 43

2.7 Need for the research 45

3 METHODOLOGY 47

3.1 Samples 47

3.2 Methods and procedures 47

3.2.1 Raw Sample Characteristics 47

3.2.2 Isotherm testing for orthophosphate and total phosphorus adsorption 49

3.2.3 Effect of pH on orthophosphate and total phosphorus removal 49

3.2.4 Desorption testing 50

4 RESULTS AND DISCUSSION 51

4.1 Characteristics of alum sludge and raw sewage 51

4.2 Temperature effects on phosphorus removal 53

4.3 pH effects on phosphorus removal 62

4.4 Desorption tests 64

5 CONCLUSIONS AND RECOMMENDATIONS 67

APPENDIX A 74

APPENDIX B 77

APPENDIX C 84

APPENDIX D 90

APPENDIX E 94

APPENDIX F 98

LIST OF TABLES

Table 2—1. Classes of phosphorus containing compounds of importance in aquatic systems (adapted from Snoeyink and Jenkins, 1980). 5

Table 2—2. Typical untreated domestic wastewater characteristics (Metcalf and Eddy, 2003). 6

Table 2—3. Typical alum sludge characteristics (UMA group, 1984). 13

Table 2—4. Comparison of thickening processes (AWWA/ASCE/EPA, 1996) 15

Table 2—5. Performance of different sludge handling systems (AWWA/ASCE/EPA, 1996). 20

Table 2—6. Sludge solids requirements for various disposal options (AWWA/ASCE/EPA, 1996). 22

Table 2—7. Performance of sludge thickening methods for different types of sludges (Alberta Environment, 2006). 29

Table 2—8. Sludge dewatering methods' performance for different types of sludges (Alberta Environment, 2006). 36

Table 4—1. Alum sludge characterization summary. 51

Table 4—2. Raw sewage characterization summary 52

Table 4—3. Percent phosphorus removal by alum sludge at room temperature reported in different studies. 57

Table 4—4. Freundlich isotherm parameter values for orthophosphate adsorption in terms of total aluminum at 5, 12, and 19°C. 61

Table 4—5. Freundlich isotherm parameter values for total phosphorus adsorption in terms of total aluminum at 5, 12, and 19°C 61

LIST OF FIGURES

Figure 2-1. Percent dry solids for treatment of coagulant sludges (ASCE/AWWA, 1998). 14

Figure 4-1. Orthophosphate removal from raw sewage at 19°C. 54

Figure 4-2. Orthophosphate removal from raw sewage at 12°C. 54

Figure 4-3. Orthophosphate removal from raw sewage at 5°C. 55

Figure 4-4. Total phosphorus removal from raw sewage at 19°C. 55

Figure 4-5. Total phosphorus removal from raw sewage at 12°C. 56

Figure 4-6. Total phosphorus removal from raw sewage at 5°C. 56

Figure 4-7. Freundlich isotherm for orthophosphate adsorption on aluminum at 19°C. .. 58

Figure 4-8. Freundlich isotherm for orthophosphate adsorption on aluminum at 12°C. .. 58

Figure 4-9. Freundlich isotherm for orthophosphate adsorption on aluminum at 5°C. 59

Figure 4-10. Freundlich isotherm for total phosphorus adsorption on aluminum at 19°C. 59

Figure 4-11. Freundlich isotherm for total phosphorus adsorption on aluminum at 12°C. 60

Figure 4-12. Freundlich isotherm for total phosphorus adsorption on aluminum at 5°C. 60

Figure 4-13. Effect of pH on orthophosphate adsorption. 62

Figure 4-14. Effect of pH on total phosphorus adsorption. 63

Figure 4-15. Specific masses of orthophosphate adsorbed at pH 7.5 and desorbed at pH 5 and 9 at 19°C. Units: mg P/g total aluminum. 64

Figure 4-16. Specific masses of total phosphorus adsorbed at pH 7.5 and desorbed at pH 5 and 9 at 19°C. Units: mg P/g total aluminum. 65

LIST OF SYMBOLS AND ABBREVIATIONS

Al	Aluminum
$AlPO_4$	Aluminum phosphate
$Al(OH)_3$	Aluminum hydroxide
ANOVA	Analysis of variance
BOD_5	5 day biochemical oxygen demand
$CaCO_3$	Calcium carbonate
COD	Chemical oxygen demand
DI	Deionized water
$FePO_4$	Ferrous phosphate
GBWWTP	Gold Bar wastewater treatment plant
ICP-AES	Inductively Coupled Plasmas in Analytical Atomic Spectrometry
P	Phosphorus
PO_4^{3-} -P	Phosphate expressed as phosphorus
PZC	Point of zero charge
PZNPC	Point of zero net proton charge
rpm	Revolutions per minute
SRT	Solids retention time
TCLP	Toxicity characteristic leaching procedure
WAS	Waste activated sludge
WTP	Water treatment plant
WWTP	Wastewater treatment plant

1 INTRODUCTION

Alum sludge consists mainly of solid aluminum hydroxide, colloidal solids and adsorbed material formed as a result of coagulation and flocculation processes during water treatment. In the coagulation process, aluminum salts used as coagulants create a gelatinous sludge that will contain aluminum hydroxide and other particles and flocculated materials (AWWA, 1999). Water treatment plants produce large amounts of alum sludge every year that must be disposed of in a responsible manner. Typical disposal methods for water treatment sludge include landfill, land application, discharge to municipal sewers and direct discharge to streams. Landfill and land disposal options require the concentration of sludge solids that can be achieved through thickening and dewatering operations (ASCE, AWWA, USEPA, 1996). However, alum sludge does not dewater easily because of its gelatinous nature. The tendency of alum sludge to adsorb phosphorus from soils, thereby reducing the phosphorus available for plant growth, limits its applicability to disposal on cropland (Kyle and McClintock., 1995; Cox et al., 1997; Ippolito et al., 2003 and Hyde and Morris, 2004). Direct discharge of alum sludge to streams is a less expensive option compared to the other methods but it can be practiced only if there is no significant negative impact on the receiving water and if alternate management options are unavailable (Alberta Environment, 2006). The water treatment industry is in search of a suitable option for disposing of waste alum sludge, which will have little or no impact on the environment and preferably will be beneficial. Disposal of alum sludge to sanitary sewers can be an attractive and inexpensive disposal option and due to the capacity of alum sludge to adsorb phosphorus, this disposal method may also be beneficial.

Phosphorus is an essential nutrient for plant growth. But when surface water receives excessive amounts of phosphorus, rapid growth of algae and other aqueous plants is observed that may lead to eutrophication (Kim et al., 2003). Eutrophication is responsible for flow retardation, fish killing, filter clogging, undesirable odor and taste of potable water and also for deterioration of recreational and aesthetic values of water bodies (Unnithan et al., 2001). Typically, phosphorus concentrations in municipal wastewater

range from 4 to 16 mg/l-P (Metcalf and Eddy, 2003). Before being discharged, the phosphorus concentration must be reduced to 1 mg/l-P specified by Alberta Environment (2006). Phosphorus can be removed from natural, domestic and industrial treatment systems by chemical precipitation, adsorption and/or biological treatment. Chemical precipitation methods are usually costly and produce high sludge volumes. In many cases, adsorption can be a less expensive alternative as it can be accomplished using inexpensive adsorbents such as fly ash, alum sludge, alumized red mud, or bauxite, activated alumina (Ugurlu and Salman, 1998; Kim et al., 2003; Mohanty et al., 2004 and Altundogan and Tumen, 2001; Hano et al., 1997). As alum sludge is generated as a waste during drinking water treatment, using alum sludge for phosphorus removal from raw wastewater has the potential to be an economical and environmentally friendly sludge management option for alum sludge.

Several studies have been conducted to investigate the performance of alum sludge on phosphorus removal (Barr, 1992; Galarneau and Gehr, 1997; Huang and Chiswell, 2000; Kim et al., 2003 and Georgantas and Grigoropoulou, 2005). In a recent study, Georgantas and Grigoropoulou (2005) showed that alum sludge, with a concentration of 75 mg/l as Al can remove orthophosphate (initial concentration 8.3 mg/l-P) from raw wastewater completely. The degrees of phosphorus removal reported in other studies show considerable variation, depending upon the characteristics of the raw wastewater and the alum sludge. The majority of these studies used synthetic alum sludge and wastewater prepared in the laboratory and did not investigate the effects of temperature and pH on phosphorus removal.

1.1 Hypothesis

The hypothesis of this research was that alum sludge as water treatment plant residual can remove phosphorus from raw sewage via the adsorption method. Two important factors; temperature and pH may influence the phosphorus removal efficiency of alum sludge. However, the adsorbed phosphorus may desorb to some extent in the environment.

1.2 Objectives

The objective of this study was to assess the ability of waste alum sludge to remove phosphorus from raw municipal wastewater. This will include investigating the effects of temperature and pH on phosphorus removal, as these factors are known to influence adsorption. Both orthophosphate and total phosphorus removal were measured in this study. Finally, the mobility of adsorbed phosphorus was studied via desorption tests.

1.3 Outline of the thesis

This thesis is organized into five chapters. Chapter 1 provides a general background and describes the importance of the thesis and the study objectives. A review of relevant literature is presented in Chapter 2. Chapter 3 provides detailed information about the materials, experimental apparatus and methodology followed to accomplish the objective of this thesis. Experimental results are presented and discussed in Chapter 4. The conclusion arising from the results and discussions in Chapter 4 are presented in Chapter 5. The appendices contain the raw data, sample calculations and the results of supporting experiments.

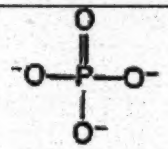
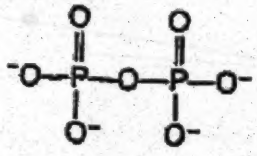
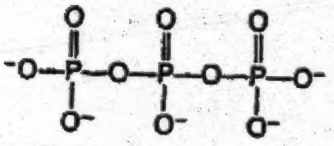
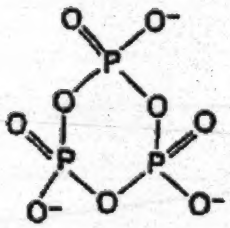
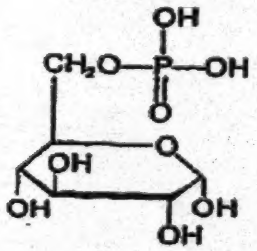
2 LITERATURE REVIEW

This chapter reviews different forms of phosphorus present in wastewater including their sources, environmental significance and the typical discharge limit specified by the regulatory agencies; general methods used for phosphorus removal; water treatment plant alum sludge and wastewater treatment plant sludge handling and disposal. It also contains a brief discussion on relevant research works involved in evaluating the capacity of fresh alum and spent alum sludge for phosphorus removal and the effect of temperature and pH on the removal efficiency.

2.1 Phosphorus in Wastewater

Phosphorus can exist in several forms in wastewater. The usual forms of phosphorus are orthophosphate, polyphosphate and organic phosphorus. The orthophosphates are the salt of phosphoric acid (H_3PO_4) and orthophosphates of concern in wastewater are sodium phosphate (Na_3PO_4), sodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), and ammonium hydrogen phosphate [$(NH_4)_2HPO_4$]. These are readily bioavailable forms of phosphorus that can cause the problems associated with algal blooms (Sincero et al., 2003). The polyphosphates are usually made up of two or more phosphorus atoms, oxygen atoms and sometimes hydrogen atoms combined in a complex molecule. Polyphosphates in wastewater are hydrolyzed to orthophosphate, although it is usually quite a slow process. Polyphosphates are important components in textile washing powders and other detergents. When organic compounds containing phosphorus are acted upon by microorganisms, they also undergo hydrolysis into the orthophosphate forms. The organic phosphate is normally not so important for domestic wastes but for industrial waste, and even for wastewater sludge, it can be an important constituent. Thus, as with all the other phosphorus species, they have to be controlled before wastewaters are discharged. Table 2-1 presents different forms of phosphorus with their structural representation and species of importance.

Table 2—1. Classes of phosphorus containing compounds of importance in aquatic systems (adapted from Snoeyink and Jenkins, 1980).

Group	Structural representation (Typical)	Species of importance	Acid ionization constants, 25°C
Orthophosphate		H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, HPO_4^{2-} complexes	$pK_{a,1} = 2.1$ $pK_{a,2} = 7.2$ $pK_{a,3} = 12.3$
Polyphosphate	 Pyrophosphate	$H_4P_2O_7$, $H_3P_2O_7^-$, $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, $P_2O_7^{4-}$, $HP_2O_7^{3-}$ complexes	$pK_{a,1} = 1.52$ $pK_{a,2} = 2.4$ $pK_{a,3} = 6.6$ $pK_{a,4} = 9.3$
	 tripolyphosphate	$H_3P_3O_{10}^{2-}$, $H_2P_3O_{10}^{3-}$, $HP_3O_{10}^{4-}$, $P_3O_{10}^{5-}$, $HP_3O_{10}^{4-}$ complexes	$pK_{a,1} = 2.3$ $pK_{a,2} = 6.5$ $pK_{a,3} = 9.2$
Metaphosphate	 trimetaphosphate	$HP_3O_9^{2-}$, $P_3O_9^{3-}$	$pK_{a,1} = 2.1$
Organic phosphate	 Glucose 6-phosphate	Many and varied, including phospholipids, sugar phosphates, nucleotides, phosphoamides, etc.	

The sources and quantities of phosphorus in domestic wastewaters vary widely from plant to plant. The general sources of phosphorus in wastewater are human wastes, industrial discharges, runoff to combined sewers and phosphate bearing detergents (Bowker and Stensel, 1990). The characteristics of raw wastewater vary considerably, but typical characteristics as described by Metcalf and Eddy (2003) are presented in Table 2-2. The approximate concentrations of the various forms of phosphorus present in typical raw domestic sewage are 5 mg /l-P, 3 mg /l-P, 1 mg /l-P and 1 mg /l-P as orthophosphate, tripolyphosphate, pyrophosphate and organic phosphate, respectively (Omiko and Vanloon, 1999).

Table 2—2. Typical untreated domestic wastewater characteristics (Metcalf and Eddy, 2003).

Parameter	Typical values
Total solids (mg/l)	390 to 1230
Suspended solids (mg/l)	120 to 400
BOD_5 (mg/l)	110 to 350
COD (mg/l)	250 to 800
Total Phosphorus (mg/l – P)	4 to 16

2.1.1 Environmental significance

Phosphorus makes a major contribution to agricultural and industrial development. However, phosphorus released to the aquatic environment can have detrimental environmental effects. Aquatic algae and plants use an inorganic form of phosphorus for their nutrition. In most lakes and rivers, phosphorus is the primary nutrient that limits the growth of algae and plants. Therefore, excessive phosphorus in a freshwater system increases plant and algal growth that can lead to increases in turbidity and oxygen depletion (Duenas et al., 2003). When there is no oxygen at the bottom of a freshwater system, phosphorus that previously had been locked in the sediment can be released to the water column. High levels of phosphorus can also promote the growth of cyanobacteria. Cyanobacterial blooms can cause a range of water quality problems

including summer fish kills, livestock, and wildlife kills, odors, and reduce the suitability of the water as a source for drinking water treatment plants (Canadian Water Quality Guidelines, 2005).

2.1.2 Phosphorus discharge limit

Galarneau and Gehr (1996) reported that, in the Canadian province of Quebec, phosphorus discharge limits vary from plant to plant but typically the effluent total unfiltered phosphorus discharge target is between 0.8 to 1 mg /l-P. A similar situation exists in Alberta, with effluent total phosphorus discharge being limited to 1 mg/l-P from municipal plants treating wastewaters from populations greater than 20,000 (Alberta Environment, 2006).

2.2 Methods of phosphorus removal

The technologies developed for phosphorus removal date back to the 1950's. Chemical precipitation, adsorption and biological processes are the methods traditionally applied for phosphorus removal.

2.2.1 Phosphorus removal by chemical precipitation

Chemical precipitation is a physico-chemical process that comprises the addition of multivalent metal salt ions to form precipitates of sparingly soluble phosphates (Metcalf and Eddy, 2003). Generally, an iron or aluminum salt such as aluminum sulfate, sodium aluminate, ferric chloride, ferrous chloride or ferrous sulfate is added to the wastewater (Bowker and Stensel, 1990). Chemical precipitation is a very complex process that involves a number of competing reactions. The stoichiometry of phosphorus precipitation by aluminum or ferric dictates that 1 mole of aluminum or iron will precipitate 1 mole of phosphate. However, the chemical requirements observed in practice exceed theoretical values due to competition from other anions in solution (Bowker and Stensel, 1990). Barr (1992) reported that an alum dose of 300 mg/l as alum could remove approximately 97%

of orthophosphate from raw wastewater having an initial concentration of 14.11 mg/l-P and pH was 7.73. The theoretical minimum solubility of $AlPO_4$ and $FePO_4$ occur at approximately pH 6.3 and 5.3, respectively. However, in practice good phosphorus removal can occur anywhere in the range of pH 6.5 to 7.0 (Metcalf and Eddy, 2003).

Phosphorus can also be removed by lime precipitation, which is basically a water softening process. When the lime is added to water it reacts with the natural bicarbonate alkalinity and precipitates $CaCO_3$. When the pH value of the wastewater is increased beyond approximately 10, excess calcium ions react with phosphate in wastewater and precipitate hydroxylapatite $Ca_{10}(PO_4)_6(OH)_2$ (Metcalf and Eddy, 2003). Removal with lime is either conducted as a single-stage or a two-stage process. In the single-stage process (low-lime system), pH is kept below 10. This process can achieve effluent total phosphorus levels of 1 mg/l-P. In the two-stage process (high-lime system), the pH is raised to between 11.0 and 11.5. This process can achieve an effluent total phosphorus concentration less than 1 mg/l-P (Bowker and Stensel, 1990).

The chemical precipitation process is the most popular, reliable, well-documented phosphorus removal technique. This process is relatively easy and inexpensive to install at existing facilities. Through this process effluent phosphorus levels can be controlled easily by metal salt dosage to maximum efficiency levels. On the other hand typical disadvantages of the chemical precipitation process include high chemical costs and production of large sludge volumes that lead to higher sludge handling and disposal costs (Bowker and Stensel, 1990).

2.2.2 Phosphorus removal by adsorption

Adsorption is also considered to be an effective method for phosphorus removal. Noll et al. (1992) defined adsorption as a process by which material accumulates at the interface between two phases. These phases can be categorized as liquid-liquid, liquid-solid, gas-liquid, and gas-solid. The adsorbing phase is called adsorbent and the substance being

adsorbed is defined as adsorbate. Generally three types of adsorption processes are available: physical, chemical and ion exchange adsorption (Sawyer et al., 2003). Physical adsorption occurs because of the operation of weak forces of attraction such as the vander Waals forces between molecules. Chemical adsorption is due to the much stronger forces comparable to chemical compound formation forces. Ion exchange adsorption is due to the electrical attraction between the adsorbate and oppositely charged sites on the adsorbent surface. Generally, ions of greater charge, such as trivalent ions, are attracted more strongly to the oppositely charged sites than are ions of lesser charge (Sawyer et al., 2003). Physical adsorption only takes place at relatively low temperatures; can occur as monolayer or multilayer adsorption; and is reversible. On the other hand chemical adsorption is irreversible; forms a monolayer; and is possible over a wide range of temperatures (Ruthven, 1984).

In many instances of engineering practice, adsorption provides the most cost effective means of removing contaminants from solution to extremely low levels. A number of different adsorbents have been investigated for phosphorus removal, including activated alumina with aluminum sulfate, aluminum hydroxide, iron hydroxide, bauxite, fly ash, and alumized red mud (Altundogan et al, 2001). Most of these adsorbents are inexpensive and easily available. Sometimes reagents are not needed to overcome high alkalinity and wastewater pH is unaffected (Morse et al., 1998). The adsorption method for phosphorus removal is relatively simple, and studies have shown that adsorption can achieve a very good percent removal of phosphorus. Ugurlu and Salman (1998) investigated phosphorus removal by adsorption onto fly ash. Their batch study showed that 20 g/l of fly ash could remove more than 99% phosphorus from a synthetic solution (prepared from stock solution 5 g P/l of anhydrous Na_2HPO_4) when the initial phosphorus concentration was 20 mg P/l at 27.8°C.

Adsorption Isotherms

The mass of material adsorbed per unit mass of adsorbent is called adsorption density. The equilibrium relationship between the adsorption density (q) and the soluble adsorbate

concentration (C) at a given temperature is called the adsorption isotherm (Benjamin, 2002). Langmuir and Freundlich isotherms are the most commonly used isotherms in phosphorus removal. Typically, the applicability of a particular isotherm depends on these factors: situation (eg; engineered reactor verses natural environment); nature, concentration and number of adsorbates (eg; hydrophobic verses hydrophilic, neutral verses charged species, high concentration verses low concentration, single contaminants verses multiple contaminants); type of adsorbent; type of fluid and other environmental factors (Sawyer et al., 2003). The basic equations of these two isotherms are described below.

Langmuir isotherm

The Langmuir isotherm assumes that a single adsorbate binds a single site on the adsorbent and all the surface sites on the adsorbent have the same affinity for the adsorbate. The basic equation developed for Langmuir isotherm is

$$q = \frac{q_m bC}{(1 + bC)} \tag{2.1}$$

Where,

q = adsorption density (mass adsorbate/mass adsorbent)

q_m = maximum adsorption density (mass adsorbate/mass adsorbent)

C = soluble adsorbate concentration (mass/volume)

b = measure of affinity of adsorbate for adsorbent.

With the increase of C values adsorption sites become filled and q approaches to q_m.

Freundlich isotherm

The Freundlich isotherm can be derived from the Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent having different affinities for different

adsorbates with each site behaving according to the Langmuir isotherm. The basic equation developed by Freundlich is

$$q = KC^{1/n} \tag{2.2}$$

Where,

q = adsorption density (mass adsorbate/mass adsorbent)

C = soluble adsorbate concentration (mass/volume)

K = measure of the capacity of the adsorbent (volume/mass adsorbent)

n = measure of how affinity for the adsorbate changes with the changes in adsorption density.

When $1/n = 1$, it indicates that all sites on the adsorbent have equal affinity for the adsorbate. If $1/n < 1$, it indicates that affinity decreases with increasing adsorption density and if $1/n > 1$ over a limited range of C values, this implies that as the adsorption density increases the affinity of the surface for the adsorbate also increases (Benjamin, 2002).

The Langmuir isotherm equation has an advantage in calculating adsorption maximum but this equation assumes that all surface sites on the adsorbent have the same affinity for the adsorbate. On the other hand, the Freundlich isotherm is derived from assuming a heterogeneous surface that has different affinities for different adsorbates with each site behaving according to the Langmuir isotherm. The Freundlich isotherm also assumes a complete absence of chemisorption and that the mass absorbed increases infinitely with concentration or pressure (Noll et al., 1992). Jamieson et al. (2002) found the Freundlich isotherm sometimes performed better than the Langmuir isotherm because of not assuming a constant binding energy. Some researchers found that the Freundlich isotherm fit the experimental data well (Ugurlu and Salman, 1998; Mohanty et al., 2004) and others found that Langmuir isotherm fit their experimental data set well (Unnithan et al., 2001; Kim et al., 2003). The fit of the isotherm model with experimental data varies depending on the experimental conditions, adsorbents, and adsorbates.

2.2.3 Phosphorus removal by biological processes

Biological phosphorus removal in the activated sludge process has become a widespread technology over the last 20 years. The generally accepted theory for biological phosphorus removal is that anaerobic-aerobic contacting results in a competitive substance utilization and selection of phosphorus storing microorganisms (Bowker et al., 1990). The basic process includes stressing of microorganisms, mainly bacteria, in an anaerobic zone followed by 'luxury uptake' of phosphorus in an aerobic zone. This phosphorus is incorporated into cell tissue that is removed in the sludge during clarification. The phosphorus then can be removed by conventional chemical precipitation, wasting the sludge, or by further biological methods (Barr, 1992). The most commonly used biological phosphorus removal processes are the Phoredox (A/O) process, A^2/O (anaerobic/anoxic/aerobic) process and UCT (University of Capetown) process (Metcalf and Eddy, 2003). In the Phoredox process, nitrification does not occur and to prevent the initiation of nitrification low operating SRTs are used. The desirable SRT values range from 2 to 3 days at 20°C and 4 to 5 days at 10°C. A^2/O provides an anoxic zone for denitrification. Use of an anoxic zone minimizes the amount of nitrate fed to the anaerobic zone in the return activated sludge. The UCT process was developed to minimize the effect of nitrate in weaker wastewaters entering the anaerobic contact zone because presence of nitrate in the anaerobic zone may affect biological phosphorus removal efficiency. In this process the return activated sludge (RAS) is recycled to the anoxic stage and the internal recycle is from anoxic to anaerobic stage. This internal recycle feature provides for increased organic utilization in the anaerobic stage. But in A^2/O process the RAS recycle is directed to the anaerobic zone.

Biological removal processes are established technologies for phosphorus removal. Typical advantages include good phosphorus removal, production of sludge with good settling characteristics. In addition, phosphorus removal can be accomplished together with ammonia nitrogen or total nitrogen removal. However, complex technology is required to install and operate these systems, and sludge handling may be more difficult (Morse et al., 1998).

2.3 Waste alum sludge: generation, handling and disposal

Alum sludge in a water treatment plant is mainly generated from coagulation and flocculation processes used to remove turbidity and/or color. In coagulation process aluminum salts are used as coagulants and they create a gelatinous sludge that will contain aluminum hydroxide and other particles and flocculated materials (Alberta Environment, 2006). Alum sludge is difficult to dewater because it is usually thixotropic and gelatinous (UMA group, 1984). Table 2-3 shows the predominant characteristics of alum sludge.

Table 2—3. Typical alum sludge characteristics (UMA group, 1984).

Parameter	Typical values
pH	5.5 to 7.5
Total solids (%)	0.1 to 4
Suspended solids (%)	75 to 99 of total solids
Aluminum (%)	4 to 11 of total solids
Total Phosphorus (mg/l – P)	0.3 to 200

2.3.1 Sludge treatment

Sludge handling includes conveyance, treatment and disposal of alum sludge. Economics, regulatory requirements and many other factors may dictate the need for the sludge treatment before disposal. Sludge treatment comprises thickening, conditioning, dewatering operations. The purpose of sludge treatment is to reduce its water content and in some cases to recover the coagulant chemical. The water content of a sludge can be categorized as: (1) free water not held by the floc; (2) floc water that is trapped within the sludge as water might be in a sponge; (3) capillary water that is retained between sludge solids by surface tension; and (4) bound water that is chemically bound to floc surfaces. The volume of Category (1) water can be reduced by thickening. Water volumes in Categories (2) and (3) can be reduced by the application of pressure as during mechanical

dewatering. Category (4) water is not affected by gravity thickening or mechanical dewatering, but can be removed by freeze-thaw conditioning.

The following solid concentrations are the normal ranges of coagulant sludge concentration achieved by various processes.

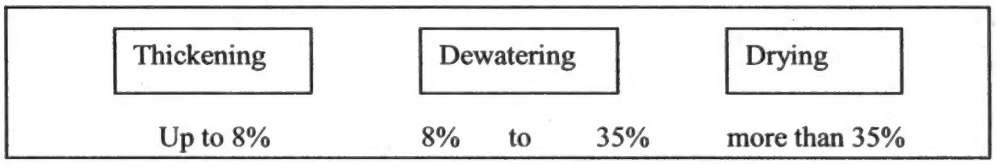


Figure 2-1. Percent dry solids for treatment of coagulant sludges (ASCE/AWWA, 1998).

Thickening

Thickening processes reduce the sludge volume and produces a more concentrated sludge. Gravity thickening, flotation thickening or gravity belt thickeners are usually used for thickening. Among them, gravity thickening is the most commonly used thickening process for alum sludge.

Gravity thickening

Gravity thickening is used for solids having specific gravity greater than 1. In this process residuals are conveyed to gravity settling tanks at a flow rate that allows the residuals sufficient retention time to settle. Thickener tanks are generally circular and usually concrete. They are typically equipped with rake mechanism to remove solids. The floors are conical in shape (with a slope of 10 to 20%), which enables more efficient solid movements to the discharge hopper. The degree of thickening generally depends on the hydroxide to total suspended solids ratio (AWWA/ASCE/EPA, 1996). Alum sludge can be conditioned with polymers that may improve the thickening by increasing particle size and reducing solids carryover in reclaimed water.

Flotation thickening

Flotation thickening is an option for thickening sludges consisting of low-density particles that can be performed either by a dissolved air flotation, dispersed air flotation or vacuum flotation processes. Each of the techniques uses air bubbles to adsorb particles and then the particles may be floated to the water surface for separation from the liquid stream. The floats are then removed by skimmers. Flotation thickening can be more applicable for sludges with high hydroxide compounds (greater than 40% by weight) and generally has not been used for long term, large scale thickening in North America. However, European facilities report concentrate hydroxide sludges to levels between 3 to 4% using dissolved air flotation (AWWA/ASCE/EPA, 1996).

Gravity belt thickeners

In this process the metallic hydroxide sludge is discharged directly onto a horizontal porous screen and as the sludge moves along the length of the screen, water is removed by gravity. Solids concentrations of 2.5 to 4.5 percent can be achieved through this process. It has a simple design and its operating cost is low. Advantages of gravity belt thickeners include simple design, low operating cost, limited operator attention and minimal chemical conditioning. On the other hand the production of two waste streams: filtrate and belt wash water, the labour required for operation and maintenance and chemical conditioning of the sludges are general disadvantages of gravity belt thickener (ASCE/AWWA, 1998). Table 2-4 shows the performance comparison for various types of thickening processes for hydroxide sludge.

Table 2—4. Comparison of thickening processes (AWWA/ASCE/EPA, 1996).

Thickening process	Solids loading (kg/day/m^2)	Solids concentration (%)
Gravity	19.5	1 to 3
Flotation	97.6	2 to 4
Gravity Belt	N/A*	2.5 to 4.5

*N/A – not applicable

Conditioning

Conditioning can improve the dewatering characteristics of alum sludge. Both chemical and physical conditioning can be used to treat water treatment plant residuals.

Chemical conditioning

Most mechanical thickening and dewatering processes include chemical conditioning. Typical chemicals used for conditioning are ferric chloride, lime or polymer. Anionic polymers with a high molecular weight are the most successful polymers.

Physical conditioning

Several physical conditioning systems such as precoat or nonreactive additives, freeze thaw conditioning and thermal conditioning at high temperatures can optimize the thickening or dewatering process. A typical precoat additive used for dewatering system is diatomaceous earth. Freeze-thaw conditioning can be done either in an open-air process in cold weather or through mechanical equipment. Reynolds and Richards (1996) reported that freezing and thawing might increase the solids content of 2% alum sludge to 20%. Alum sludge may be conditioned in reactors at elevated temperature (350 to 400°F) and pressure (250 to 400 psi) to release the bound water. This method is usually effective in the presence of organic matter in solids (AWWA/ASCE/EPA, 1996).

Dewatering

Dewatering is mainly the separation of liquid from solids. This process is more difficult for alum sludge than for a sludge generated from a water softening process. Dewatering can be done by non-mechanical or mechanical means.

Non-mechanical dewatering

Non-mechanical dewatering systems are easier to operate and also require less energy to operate than mechanical systems. But this process is used in locations where sufficient land is available and where it can be economical as well as effective for sludge treatment. Lining of dewatering basin to protect an underlying aquifer is a common practice. Sand drying beds, freeze-assisted sand beds, solar drying beds, vacuum-assisted drying beds, wedgewire beds and lagoons are general forms of non-mechanical dewatering (ASCE/AWWA, 1998).

Sand drying beds

Dewatering on the sand bed occurs through gravity drainage of free water followed by evaporation to the desired solids concentration levels. The rate of evaporation varies with local climatic conditions and the solid surface characteristics. Sand drying beds are developed primarily for wastewater treatment plant residuals but are now commonly used for water treatment residuals. Alum sludges generally attain solids concentration of 15 to 30% with this process. Usually alum sludges require 3 to 4 days to drain, but polymer may accelerate this to 1.5 to 3 days. The drying time depends on the depth at which sludge may be applied. For coagulant sludge the depth usually ranges from 0.2 to 0.76 m. It was reported in ASCE/AWWA (1998) that alum sludge required 20 hours per percent solids concentration for a 0.2 m application but it required 60 hours per percent solids concentration for a 0.41 m application.

Freeze-Assisted sand beds

The climatic condition of alternate freezing and thawing can also release the bound water from alum sludge. Freezing alum residuals changes the structure of the solids; it compresses the solids into large discrete conglomerates surrounded by frozen water. After thawing, drainage occurs quickly through the large pores and channels created by the frozen water. Freezing can be done by mechanical or natural means, with natural

freezing being used most frequently considering the high cost associated with mechanical systems (ASCE/AWWA, 1998).

Solar drying beds

The total bed area for solar drying beds must be greater than that of conventional sand beds to achieve the same dewatering results in the same period. The main advantage of this process is the ability to use relatively heavy equipment for solids removal (ASCE/AWWA, 1998).

Vacuum-Assisted drying beds

In this process, a vacuum is applied to the underside of a rigid, porous media plate and the vacuum draws free water through the plates and essentially all the sludge solids are retained on top, forming a cake of fairly uniform thickness. The concentrated solids can be between 11% and 17% and it depends upon the type of solids and the kind and amount of conditioning agents used (ASCE/AWWA, 1998). Improper conditioning using the wrong polymer, poor mixing and also incorrect dose may cause poor performance of the bed. If the plates are not cleaned properly they may clog and this can result in poor performance.

Wedgewire beds

This process is physically similar to the vacuum-assisted drying beds. The medium of this process consists of a septum with wedge shaped slots about 0.03 cm wide (ASCE/AWWA, 1998). This septum supports the sludge cake and allows drainage through the slots. Through a controlled drainage process a small hydrostatic suction is exerted on the bed and removes water from the sludge.

Lagoons

Lagoons can be used for storage, thickening, dewatering, drying or even, sometimes, as a final disposal option. Dewatering process with lagoons is similar to the sand drying process but it can operate at a much higher initial loading. Sludges are added to the lagoon until it is full. The sludge settles, free water is withdrawn, and the sludge is allowed to air dry. This method can achieve a solids content of up to approximately 10% for metal hydroxides (ASCE/AWWA, 1998).

Mechanical dewatering

Mechanical devices commonly used for dewatering are belt filter presses, centrifuges, filter presses and vacuum filters, although vacuum filters have no use in alum sludge dewatering (AWWA, 1999).

Belt filter presses

Dewatering of alum sludge is very difficult because of its gelatinous nature. Belt filter presses can dewater the alum sludge and usually the percent solids contents achieved through the dewatering depends on the source of the water coagulated with alum. This process can dewater to 15 to 20% solid contents and it can be improved by chemical conditioning with polymer, which produces a large, strong floc and drains the free water easily (ASCE/AWWA, 1998). The major advantages of this process are low energy consumption compared to other mechanical processes, experience process and competitive price. On the other hand high attention of operator and comparatively difficult odour control are typical disadvantages of this process.

Centrifuges

Centrifugation of sludge is basically a shallow-depth settling process enhanced by applying centrifugal force. The solid bowl (scroll or decanter) centrifuge is widely used for water plant sludge dewatering (AWWA, 1999). Generally, continuous feed operation,

minimal operators' attention, 20 to 30 percent solids cake production and low maintenance requirements are considered as the advantages of this process.

Filter presses

Generally a filter press can produce the highest final cake concentration of any of the mechanical dewatering devices. The equipment commonly used to dewater WTP residuals is either the fixed-volume recessed plate filter or the diaphragm filter press. Dewatering of alum sludge requires lime as a conditioning agent. It can achieve the cake solid concentration ranging from 30 to 60 percent; however it depends on the source of the alum residual (AWWA/ASCE/EPA, 1996). High quality filtrate production, good mechanical reliability and adaptability with varying influent solids concentration are the typical advantages of this process. But it has some disadvantages, such as, relatively high construction and operating costs. Table 2-5 represents the performances of various types of dewatering processes of coagulant sludges.

Table 2—5. Performance of different sludge handling systems (AWWA/ASCE/EPA, 1996).

Dewatering process	Solids concentration (%)
Gravity thickening	3 to 4
Scroll centrifuge	20 to 30
Belt filter press	20 to 25
Vacuum filter	25 to 35
Pressure filters	35 to 45
Diaphragm filter press	30 to 40
Sand drying beds	20 to 25
Storage lagoons	7 to 15

Drying

The drying of dewatered water treatment plant residuals can reduce the transportation and disposal costs of WTP sludge by reducing solids volume and water content. Drying to solid concentration greater than 35% is a regulatory requirement for some areas. For instance, the State of California requires that the solids concentration of a WTP waste be at least 50% before disposal to a landfill (ASCE/AWWA, 1998). Like the dewatering process, open air drying and mechanical drying processes are the most common processes for drying.

Open air drying

Either solar drying or lagoon procedures may be applied to the drying process. Drying depends on evaporation to achieve the desired solids concentrations; sometimes an extended drying process is needed. One method of accelerating drying is to use a tractor to periodically furrow and mix the solids to increase exposure to sun and air.

Mechanical drying

Thermal drying of solids from WTPs has not been practiced at full-scale in the United States. Steam heated dryers have shown the potential to raise the solids concentration of dewatered metal hydroxide sludge to the 65% to 75%, but this process is again untried in full scale operation (AWWA/ASCE/EPA, 1996).

Alum recovery

Alum recovery and re-use at the water treatment plant is not commonly used, but acidification with sulfuric acid can recover some alum as shown in reaction 2.3.

$$2\ Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O \qquad (2.3)$$

The supernatant containing alum is separated from the solid and can be used as liquid coagulant.

The major concerns of this handling process include recovery cost and recycle of organics and heavy metals. However, it may be feasible to recover water treatment plant alum sludge for re-use at a wastewater treatment plant utilizing chemical precipitation of phosphorus (Alberta Environment, 2006).

2.3.2 Disposal

After thickening and dewatering, the alum sludge needs to be disposed of by a proper disposal method. Typical disposal methods for water treatment sludges include landfill, land application, discharge to a municipal sewer, and direct discharge to receiving waters. The available disposal option also influences the degree of thickening and dewatering required. Typical ranges of solid contents required for the various disposal options are summarized in Table 2-6.

Table 2—6. Sludge solids requirements for various disposal options (AWWA/ASCE/EPA, 1996).

Disposal method	Solid content (%)
Land application	< 1 to 15
Landfill (co-disposal)	15 to 25
Landfill (monofill)	> 25
Residual reuse	< 1 to > 25
Discharge to sewer	< 1 to 8
Direct stream discharge	< 1 to 8

Landfill

Landfill has been one of the most commonly used disposal options for alum sludge (Hyde et al., 2004). Landfill disposal can be done in four ways: co-disposal with municipal solid waste (refuse), use as a daily landfill cover extender, monofill of water treatment residuals, and co-disposal with wastewater treatment plant residuals

(AWWA/ASCE/EPA, 1996). Landfill performance and protection of public health and the environment are the two major concerns for landfill site selection. There are some sites that are restricted from use for a landfill, such as, in or near airports, floodplains, wetlands, fault areas, seismic impact zones and unstable areas. Monofill design criteria require that the construction of a landfill will not adversely affect surrounding floodplains or air quality and will not create disease or safety threats. The major sludge monofill methods are trench filling and area filling. Trench filling is again subdivided into narrow trench and wide trench. Sludge solids content, sludge stability, site hydrogeology, ground slope and land availability will determine which monofill method should be adopted. Co-disposal of WTP residuals with municipal solid waste follows minimum technology based standards for landfill, which require a composite liner system consisting of an upper geomembrane liner and lower compacted-soil liner. The geomembrane liner minimizes the exposure of the compacted soil liner and thus it reduces the volume of leachate reaching the soil liner. The major environmental concern in the siting, construction and operation of residuals monofill is the potential for ground water contamination through the leaching of metal constituents in the residuals. The toxicity characteristic leaching procedure (TCLP) as the indicator of toxicity in a waste is used to identify and quantify the contaminants that leach from a solid waste. Cornwell et al. (1992) reported that the results of TCLP test, performed on alum sludge from two different sources, indicated no toxicity effect. Lysimeter testing provides information about the mobility of metals from WTP residuals and this test indicated that, not only, do the WTP residuals contain small concentration of metals but, also, a small portion of these metals tend to leach (Cornwell et al., 1992). These findings indicated that alum sludge disposal in a landfill can be an environmentally sound option but the integrity of landfill components can be threatened by careless or inappropriate operations.

Land application

The dewatered alum sludges can be disposed by application to agricultural lands, silviculture, land reclamation and dedicated land disposals. This process is considered as an attractive option because of its relatively low costs and potential as a long term

disposal solution (Lucas et al., 1994). However, the high adsorptive capacity of alum sludge for phosphorus, which may result in reducing the plant available phosphorus from soil, limits the application of this technique. (Kyle et al., 1995; Cox et al., 1997; Ippolito et al., 2003 and Hyde et al, 2004). There are some other draw backs of land application disposal of alum sludge, such as, increasing the concentration of metals in the soil and possibly in ground water, excessive applications of nitrogen that may result in nitrogen being transported to the ground water and the possible effects caused by the application of poorly crystallized solids of aluminum. In agricultural land application, alum sludge can improve the physical characteristics of soil but it can inhibit the plant growth. Generally, the maximum loading rate of WTP alum sludge is 2.2 to 4.4 kg dry solids/m^2 to avoid phosphorus depletion (Cornwell et al., 1992). Liquid alum sludge can be applied with a liquid manure spreader or with conventional irrigation equipment. Silviculture is the establishment, growth, reproduction and care of forest trees as a crop. Although, alum sludge application to silviculture might have the same effects as agricultural land application, studies showed that the long term application of alum sludge did not have any significant effect on soil characteristics, ground water characteristics or pine growth (AWWA/ASCE/EPA, 1996). In land reclamation, alum sludges can control runoff of excess phosphate into surface waters but care must be taken to ensure a suitable site for alum sludge application and the protection of public health and the environment. The land application site should be evaluated with the cost associated with the site, the potential social and environmental impacts on the site and the cost of dewatering and hauling.

The transportation of the alum sludge depends on whether the type of sludge is liquid or cake. Liquid sludge can be transported either by pipeline or by truck. Pipeline offers the convenience of transporting residuals regardless of weather or other external factors but pipelines go to one location and thus limit the options for land application. On the other hand truck transportation offers WTPs more options for land application and, thus, most land application programs use this method for transportation.

Discharge to sanitary sewers

Disposal of alum sludge into the sanitary sewer system can be an effective alternative. Many water utilities discharge the WTP residuals to a sewer and/or to a WWTP. This option is very attractive as well as cost effective. This disposal option can be beneficial as alum sludge with its high adsorptive capacity can remove phosphorus from wastewater (Barr, 1992; Galarneau and Gehr, 1997; Huang and Chiswell, 2000; Kim et al., 2003 and Georgantas and Grigoropoulou, 2005). In some cases, the receiving WWTP benefits from increased removal of suspended solids and or biochemical/chemical oxygen demand (BOD/COD). However, before implementing this disposal option, the solids handling capacity of the wastewater treatment plant must be assessed (AWWA, 1999). Each year a large amount of dry solids, around 4,810 tonnes sludge is produced in Rossdale water treatment plant (EPCOR annual report, 2005). On the other hand Gold Bar wastewater treatment plant is producing 18,438 dry tonnes of sludge annually (Edmonton annual report, 2001). So, the disposal of water treatment alum sludge to raw sewage may increase the solids loading by around 26%, which may overload the existing wastewater treatment facilities. In addition, the following things need to be considered; (i) the type and characteristics of WTP residuals to be discharged to the WWTP, (ii) the manner in which the residuals will be conveyed without excessive solids deposition (typical conveyance systems include gravity sewers, pumping/force mains and truck hauling) and (iii) the points at which WTP residuals are introduced to the WWTP for processing. Finally, the performance of the unit treatment processes at the WWTP must be maintained to ensure the final effluent discharge to the receiving water body is not adversely affected.

Direct discharge to surface water

Direct discharge of alum sludge to surface waters is another disposal technique practiced in some USA and Canadian jurisdictions. It is a low cost disposal option and easy to operate but it is permitted only in cases where minimal environmental effects can be demonstrated (Alberta Environment, 2006). It has been reported that the receiving water chemistry can minimize the toxic effects of metals in the discharged waste stream.

Hardness, alkalinity, pH, dissolved oxygen, sulfate and other water quality parameters can minimize the inhibitory effects of heavy metals. Direct disposal to acidic receiving water (pH less than 6) should be avoided because this may increase solubility of metals and, thus, increase the toxic affects. Aluminum has been found to not inhibit organism growth or survival (AWWA/ASCE/EPA, 1996). However, chemical characteristics and quantities of the receiving water and waste stream must be determined before disposal in order to anticipate the chemical changes to the water downstream from the point of discharge. To fully evaluate the toxicity effect, a series of toxicity tests should also be conducted on a variety of aquatic organisms that are indicative of the organisms inhabiting the aquatic system.

2.4 Wastewater treatment solids: generation, handling and disposal

Wastewater treatment plant sludges can be categorized as organic, inorganic or chemical sludges. Inorganic sludges result from grit removal operations, and contain little putrescible material. Organic sludges contain metals, nutrients, salts, organic solids, saprophytic micro-organisms and pathogenic micro-organisms (Alberta Environment, 2006). Chemical sludges such as lime and alum result from enhanced coagulation and precipitation wastewater treatment (Reynolds and Richards, 1996). The quantity and quality of sludges depend on the characteristics of the wastewater being treated and the treatment methods employed.

2.4.1 Sludge treatment

Wastewater treatment sludge requires processing in order to reduce its volume and to stabilize biodegradable organic matter. Thickening, stabilization, conditioning, dewatering, heat drying and incineration are the most common steps for sludge treatment.

Thickening

The thickening process increases the solids content of sludge and reduces the sludge volume by removing a portion of the liquid fraction. Gravity thickening and air flotation thickening are the most commonly practiced thickening methods. Alternatively, centrifuges, gravity belt thickeners and rotating drum thickeners are also used for thickening (Metcalf and Eddy, 2003).

Gravity thickening

Gravity thickening is the most common thickener process and is most effective for solids having a specific gravity greater than 1. Normally thickening is done in a circular tank and dilute sludge is fed to a center feed well. The feed sludge is allowed to settle and compact and thickened sludge is withdrawn from the conical tank bottom. The thickened sludge is pumped to digesters or dewatering equipment as required. Gravity thickeners are designed on the basis of solids loading and thickener overflow rate. Recommended maximum hydraulic overflow rates range from 15.5 to 31 m^3/m^2-d for primary sludges, 4 to 8 m^3/m^2-d for waste-activated sludge and 6 to 12 m^3/m^2-d for combined primary and waste activated sludge (Metcalf and Eddy, 2003). The degree of thickening depends mainly on the nature of sludge, as shown in Table 2-7. This thickening process is mainly used for primary sludge, and mixtures of primary and waste activated sludges, and is used rarely for waste activated sludge alone (Alberta Environment, 2006).

Air flotation thickening

Dissolved air flotation thickening can be used if the specific gravity of sludge solids is near to 1 (Reynolds and Richards, 1996). In dissolved air flotation, air is introduced to a solution that is being held at an elevated pressure. When the solution is depressurized, the dissolved air is released as finely divided bubbles that attach to sludge particles and carries them to the surface, where they are removed. Flotation thickening can successfully thicken light waste activated sludges. Other sludges such as primary sludge, trickling filter humus, aerobically digested sludge, and sludges from chemical treatment

have been flotation thickened. The use of polymers as a flotation aid can increase the solids recovery in the floated sludge from 85% to 98 or 99% and reduce the recycling loads. Polymer doses for thickening waste activated sludge are 2 to 5 kg of dry polymer per Mg of dry solids (Metcalf and Eddy, 2003). The solids content of waste activated sludge is usually higher in air flotation thickening compared to the gravity thickening, as shown in Table 2-7.

Centrifugal thickening

Centrifuges are used for thickening and dewatering sludges. Centrifugal thickening is limited normally to waste activated sludge. The settling of sludge particles is conducted under the influence of centrifugal force. Solid bowl centrifuges are the basic types of centrifuges. This thickening process is usually attractive only at facilities having capacity larger than 0.2 m^3/s, where space is limited and skilled operators are available, or for those sludges that are difficult to thicken by more conventional methods. Polymer can be used here to enhance the process and the typical polymer dose for waste-activated sludge ranges from 0 to 4 kg of dry polymer per Mg of dry solids (Metcalf and Eddy, 2003).

Gravity belt thickening

In gravity belt thickening the sludge, conditioned with polymer, is fed into a feed/distribution box in one end, where sludge is distributed evenly across the width of the belt. The water drains through the belt as the concentrating sludge is carried toward the discharge end of the thickener. The gravity-belt thickener has been used for thickening waste-activated sludge, anaerobically and aerobically digested sludge and some industrial sludge. Polymer addition is required.

Rotary-Drum thickening

Rotary media-covered drums are also used for thickening. A rotary-drum thickening system consists of a conditioner system and rotating cylindrical screens. The conditioned sludge passes to rotating screen drums, which separate the flocculated solids from the

water. Some designs also allow coupling of a rotary drum unit to a belt filter press for combination of thickening and dewatering. It can be used as a pre-thickening step before belt press dewatering and is typically used in small to medium sized plants for waste activated sludges.

Table 2—7. Performance of sludge thickening methods for different types of sludges (Alberta Environment, 2006).

Thickening method	Sludge type	Solids content achieved (%)
Gravity	Raw primary	8 to 10
	Raw primary and waste activated	5 to 8
	Waste activated	2 to 3
	Digested primary	8 to 14
Dissolved Air Flotation	Waste activated	4 to 6

Stabilization

Stabilization ensures that little bacterial decomposition will take place in the stabilized sludge. The process also improves the sludge dewatering characteristics and reduces odor generation. Anaerobic or aerobic digestion is commonly practiced for sludge stabilization (Alberta Environment 2006). Other processes such as, lagoons, wet combustion, chemical treatment and composting can also be used for sludge stabilization (Reynolds and Richards, 1996).

Anaerobic digestion

Anaerobic digestion is among the oldest processes used for the stabilization of solids and biosolids. It involves the decomposition of organic matter and inorganic matter in the absence of molecular oxygen. So, digestion reduces the solids content of an organic sludge; can reduce its pathogenic organism content; and improves its dewatering

characteristics. In many cases anaerobic digestion of municipal wastewater sludge can produce sufficient digester gas to meet most of the energy needs for plant operation. Generally three types of chemical and biochemical reactions are involved in anaerobic digestion process, such as, hydrolysis, fermentation or acidogenesis and methanogenesis. Anaerobic digestion is carried out in sealed digester vessels at operating temperatures near 35 to 37°C over a period of 15 to 30 days (Alberta Environment, 2006).

Aerobic digestion

Aerobic digestion can be used to stabilize waste activated sludge only, mixtures of waste-activated sludge or trickling filter sludge and primary sludge. Previously, aerobic digestion has been used primarily for plants of a size less than 0.2 m^3/s but presently it is being involved in larger wastewater treatment plants with a capacity of up to 2 m^3/s. According to Alberta Environment (2006), aerobic digesters should be designed to achieve a minimum sludge age of 45 days and aeration rate of 0.85 $l/m^3.s$ should be provided for diffused aeration with a minimum bottom velocity of 0.25 m/s. Minimum sludge age and air requirements need to be increased for primary sludge treatment. Aerobic digestion has some advantages over the anaerobic digestion such as, lower BOD concentrations in supernatant liquor; production of an odorless, humus-like biologically stable end product; recovery of more basic fertilizer values in the sludge; relatively easy operation; low capital cost etc. On the other hand, aerobic digestion process has some disadvantages, such as, high power cost associated with the required oxygen supply; digested biosolids products having poor dewatering capacity; no recovery of methane as a useful byproduct (Metcalf and Eddy, 2003).

Lagoons

Lagoons are generally used as a step to treat digested sludge, not as the primary means of sludge digestion. Digested biosolids can be stored in sludge lagoons for several months to facilitate solids separation.

Wet combustion

Wet oxidation uses chemical combustion of sludge under wet conditions with oxygen. The pressure used in the process can be 6900 to 12400 kPa. Injected stream raises the temperature of the sludge to about 260°C, after which combustion is generally self-sustaining. The chemical oxidation or combustion that occurs is not complete, although the treated sludge in wet combustion is sterile and dewaters easily (Reynolds and Richards, 1996).

Chemical treatment

Generally lime and chlorine have been used to stabilize the primary and secondary activated sludges. In lime stabilization process sufficient lime is added to raise the pH to 12 or higher so that biological activity is hindered, otherwise it will lead to odor production and vector attraction. This process can also inactivate viruses, bacteria and other microorganisms. The disadvantage of this process is it will increase the product mass by the addition of alkaline matter (Metcalf and Eddy, 2003). On the other hand chlorine is a very strong oxidizing agent and using 2000 mg/l chlorine can produce stable sludge that dewaters well on drying beds. The pH of this process will be 2, and prior to the dewatering by mechanical methods it should be neutralized. Otherwise low pH will interfere later with the required chemical conditioners. Another consideration is that high concentrations of chloramines need to be removed by dewatering methods (Reynolds and Richards, 1996).

Composting

Composting is a cost effective and environmentally sound alternate process for the stabilization of wastewater biosolids. In this process, organic material undergoes biological degradation to a stable end product. As the organic material in the sludge decomposes the compost heats to temperatures in the pasteurization range of 50 to 70°C and enteric pathogenic organisms are destroyed. Properly composed biosolids may be used as soil conditioners in agricultural and horticultural applications. Composting may

be accomplished under an anaerobic or aerobic condition but essentially all municipal wastewater biosolids composting was conducted under aerobic condition. Aerobic conditioning accelerates material decomposition, results in the higher rise in temperature necessary for pathogen destruction and minimizes the potential for nuisance odor.

Conditioning

Prior to dewatering, conditioning is done to enhance the dewatering process. Usually two approaches are used for conditioning. These are physical conditioning, such as, heat treatment and freeze-thaw conditioning and chemical conditioning involving the addition of either organic or inorganic chemicals.

Chemical conditioning

Organic polymers (polyelectrolytes) and inorganic coagulants (ferric chloride, lime and alum) are usually used in chemical conditioning of sludge. Use of inorganic coagulants in conditioning can be responsible for charge reduction, enmeshment in the hydroxide precipitate and also chemical bridging. However, if the sludge is to be incinerated, the use of polymers is better than that of an inorganic coagulant because the latter decreases the fuel value of treated sludge (Reynolds and Richard, 1996). Chemical conditioning of sludge and biosolids for dewatering is economical because of the increased yield and greater flexibility obtained. If the incoming moisture content is around 90 to 99% then chemical conditioning can reduce it up to 65 to 85% depending on the nature of solids to be treated (Metcalf and Eddy, 2003). The type and doses of chemicals used for conditioning depend on the properties of solids, the type of mixing and the dewatering devices to be used. Initially bench and pilot testing can be used for the selection of most suitable chemicals and dose requirements for sludge conditioning.

Physical conditioning

Heat treatment can be used to condition waste activated sludge. The sludge is usually subjected to high temperature (175 to 204°C) and pressure (1700 to 2800 kPa) that cause

hydrolysis of the water-solids matrix and breakdown biological cells. This will destroy the gelatinous characteristic of organic solids and can improve the water-solids separation characteristics (Alberta Environment, 2006). The supernatant from the heat treatment unit is high in BOD and may require treatment before the disposal to a mainstream wastewater treatment process. The processed sludge normally needs no chemical conditioning and the process is relatively insensitive to change in sludge composition. This process faces some problems, such as, high capital cost due to its mechanical complexity and the use of corrosion-resistant materials, produces side streams which are odorous and also contain high concentration of organics, ammonia, nitrogen and color, and possible scale formation in the heat exchangers, pipes and reactors (Metcalf and Eddy, 2003).

Natural freezing of water and wastewater treatment plant residuals in cold climates enhances their dewatering capacity. Freezing and thawing convert the jelly like consistency of residuals to granular type material that drains easily. Mechanical freeze-thaw systems work on difficult to dewater and waste activated sludge. In this process sludge has to be frozen for at least 30 minutes at temperature of -10 to -20°C. After thawing and dewatering, the sludge cake can range from 25 to 40% solids (Metcalf and Eddy, 2003). This process is more commonly used for water treatment plant residuals than it is for sewage treatment sludges.

Dewatering

The goal of dewatering is to remove as much water as possible from thickened and conditioned sludge. The extent of dewatering required is largely influenced by the ultimate sludge disposal method and also by the characteristics of the sludge.

Centrifugation

Centrifugation is widely used in industry to separate liquids of different density, to thicken slurries, and to remove solids. Solid-bowl centrifuge and high-solids centrifuge

are used for dewatering. However solid-bowl centrifuge is also used for thickening sludges. In the solid-bowl machine, sludge is fed at a constant flow rate into the rotating bowl, there it separates into the dense cake containing the solids and a more dilute stream called 'centrate'. It can dewater the sludge without any prior chemical conditioning but chemical conditioning using a polymer can improve the dewatering quality. A high-solids centrifuge is a modified solid-bowl centrifuge that is designed to produce a dryer solids cake. This process can achieve solids contents in excess of 30% in dewatering municipal wastewater sludges, but it may require greater polymer use (Metcalf and Eddy, 2003).

Belt filter press

The belt filter press is one of the predominant dewatering processes. It is a continuous-feed dewatering process that is based on the principles of chemical conditioning, gravity drainage and mechanically applied pressure to dewater sludge. This process is effective for almost all types of municipal wastewater sludge and biosolids (Metcalf and Eddy, 2003).

Filter presses

In this process, sludge is subjected to high pressure (690 to 1550 KPa, for chemical conditioned sludge) that forces the water out. Fixed-volume and variable-volume recessed-plate filter presses are most commonly used filter presses for dewatering. Filter press can achieve high concentration of cake solids, good filtrate clarity, and high solids capture. On the other hand mechanical complexity, high chemical costs, higher labor costs and limitation of filter cloth life are the typical disadvantages of this process (Metcalf and Eddy, 2003).

Sludge drying beds

Sludge drying beds are generally used for dewatering digested biosolids and settled sludges from plants using the extended aeration activated sludge treatment process without pre-thickening. After drying, the solids are removed and either disposed in a

landfill or used as soil conditioner. This is a low cost process. Infrequent attention is required and high solids content is achieved in the dried product. On the other hand the disadvantages of this process include large space requirements, the uncontrollable effects of climatic conditions on the drying characteristics, labor intensive sludge removal, and the potential to attract insects and produce odors. Conventional sand, paved, artificial media, vacuum assisted and solar drying beds are the different types of drying beds used for dewatering (Metcalf and Eddy, 2003).

Lagoons

Lagoons can be a substitute for drying beds for the dewatering of digested sludge. The performance of lagoons is affected by climate; precipitation and low temperatures inhibit dewatering. Lagoons are more applicable in areas with high evaporation rates because evaporation is the prime mechanism for dewatering in lagoons. The supernatant is recycled to the treatment facility and the biosolids are removed mechanically. The cycle time for lagoons varies from several months to years, but typically the biosolids are pumped to the lagoons for 18 months then the lagoon is rested for 6 months.

Heat Drying

In this process heat is applied to evaporate water and to reduce the moisture content of biosolids below the level achieved by conventional dewatering process. Sludge drying occurs in direct dryers at a temperature of approximately 370°C, whereas complete incineration requires temperatures ranging from 650 to 760°C. Typical advantages achieved through this process are reduced product transportation costs, further pathogen reduction, improved storage capability and marketability (Metcalf and Eddy, 2003).

Incineration

Incineration process converts the organic solids to oxidized end products, primarily carbon dioxide, water and ash. The ash is usually disposed in a sanitary landfill. Sludges processed by incineration are usually dewatered, untreated sludges. Normally

stabilization prior to incineration is not required for sludges. Two types of incinerators used are multiple hearth type and fluidized bed incinerator. The advantages of incineration include maximum volume reduction, thereby lessening disposal requirements, destruction of pathogens and toxic compounds and energy recovery potential. On the other hand it has some disadvantages such as high capital and operating cost, highly skilled operating and maintaining staffs are required, the residuals produced may have adverse environmental effects (Metcalf and Eddy, 2003). Fly ash collection and odor control are two important control measures associated with this process.

Table 2-8 summarizes typical solids contents achieved by the various dewatering methods when applied to various sludge types.

Table 2—8. Sludge dewatering methods' performance for different types of sludges (Alberta Environment, 2006).

Dewatering method	Solids capture (%)	Solids concentration (%)
Filter press	90 to 95	Raw primary and WAS: 30 to 50 Digested primary and WAS: 35 to 50 WAS: 25 to 50
Centrifuge (Solid Bowl)	95 to 99	Raw or digested primary and WAS: 15 to 25 WAS: 12 to 15
Belt Filter Press	85 to 95	Raw or Digested Primary and WAS: 14 to 25 WAS: 10 to 15

2.4.2 Disposal

A number of methods have been used for biosolids disposal, such as, ocean dumping, sanitary landfill, incineration, permanent lagoon storage and land application (Alberta Environment, 2006). The more commonly used disposal alternatives are landfill and land application.

Land application

Land application of biosolids is defined as the spreading of biosolids on or below the surface of soil (Metcalf and Eddy, 2003). Generally biosolids can be applied to the agricultural land, forested land, disturbed land and dedicated land disposal sites. In Alberta, the most prevalent method of sludge disposal is by land application on agricultural lands. Usually the sunlight, soil microorganisms and desiccation combine to destroy pathogens and many toxic organic substances. Trace metals are trapped in the soil matrix and nutrients are taken up by plants and converted to useful biomass. Land application of biosolids to agricultural land can be a beneficial disposal method because organic matter improves soil structures, tilth, water holding capacity, water infiltration and soil aeration. Nutrients in the biosolids can also act as a partial replacement for expensive chemical fertilizer. Land application to forested land has been also recognized as being beneficial for forest growth. Site selection is an important step for land application and usually the selection criteria depends on topography, soil characteristics, depth to ground water and accessibility and proximity to critical areas. Again, the application methods selection criteria depend on the characteristics of biosolids (liquid or dewatered), site topography and the type of vegetation present. Liquid biosolids (upper limit for solid concentration is generally 12%) can be applied to the land by vehicular application or by irrigation methods. Dewatered biosolids are spread most commonly using tractor mounted box spreaders or manure spreaders followed by plowing or disking into the soils. Bulldozers, loaders and graders may be used for high application rates. Sludge application rates should be designed to meet the nitrogen or phosphorus requirements of the surface vegetation and not exceed metal loading limits (Alberta Environment, 2001).

Landfill

Landfill has been used commonly for bio-solids disposal and is defined by Reed et al. (1987) as a method where sludge or a mixture of sludge and other solid wastes are deposited in a dedicated area and buried beneath a soil cover. Dewatering of biosolids is usually required to reduce the volume to be transported and to control the generation of

leachate from the landfill. Solid concentration is an important factor to determine the acceptability of biosolids in landfill, and depends on the quantities of sludge to be disposed of in relation to the quantities of municipal refuse, characteristics of the site itself and the expected effect of the liquid addition to the site. With small quantities of sludge for co-disposal landfilling with municipal solid waste, liquid sludge at solids concentrations as low as 3% may be accepted, but material for sludge only landfilling should contain at least 15% solids in order to physically support the soil cover and earth moving equipment (Alberta Environment, 2006). In Alberta, the municipal sludges landfilling requirement is dictated by Public Health regulations. In a sanitary landfill, the wastes are deposited in a designated area, compacted in place with a tractor or roller, and covered with a 350 mm layer of clean soil. Nuisance conditions such as odors and flies can be minimized with daily coverage of the newly deposited waste (Metcalf and Eddy, 2003).

2.4.3 Bio-solids handling and disposal in the Gold Bar wastewater treatment plant

Primary sludge and thickened activated sludge are the two major sources of sludge at the Gold Bar wastewater treatment plant. Waste activated sludge is thickened earlier with six dissolved air flotation (DAF) units using polymer and compressed air. Both of these sludges are pumped into mesophilic anaerobic digesters (sludge maintained at 37°C), where they are retained for 15 hours. The digested sludge, termed biosolids, is pumped to lagoons at the Clover Bar solid waste management facilities for further stabilization. Solid-liquid separation occurs in these lagoons, and the supernatant is returned to the Gold Bar plant for treatment. The solids are then applied to the farmland or centrifugally dewater and co-composted with municipal solid waste, or composted separately with wood waste (Heisse, 2006).

2.5 Use of alum sludge for phosphorus removal from municipal wastewater

Several studies have evaluated the effectiveness of using alum sludge in removing phosphorus from municipal wastewater. Barr (1992) conducted jar tests using alum and alum sludge to remove phosphorus from raw wastewater collected from the Gold Bar wastewater treatment plant. The jar tests were conducted using 30 seconds of rapid mixing at 100 rpm followed by 20 minutes of flocculation mixing at 30 rpm and 30 minutes of settling. The initial orthophosphate concentration of the raw wastewater ranged from 10 to 14 mg/l-P. The pH during the experiments was approximately 8. Barr reported that an alum sludge dose of 750 mg Al/l as alum could remove 75% of the orthophosphate from the raw wastewater. He also showed that using alum sludge in combination with fresh alum enhanced the orthophosphate removal. Adding alum sludge dose of 75 mg Al/l as alum with alum dose of 75 mg/l $Al_2(SO_4)_3.14H_2O$ the orthophosphate removal increased from 47% to 72%, while 47% removal was achieved by 75 mg/l alum alone. However, he also showed that when a high concentration of alum (150 mg/l $Al_2(SO_4)_3.14H_2O$) was used, the addition of alum sludge did not make any difference in orthophosphate removal. He suggested that at low dosing levels, the alum sludge enhanced suspended solids settling and thus it reduced the phosphorus levels because small colloidal particles were being removed. But as the alum dose was increased it was available in sufficient quantity to precipitate phosphorus and remove the solids without the help of additional alum sludge.

Galarneau and Gehr (1997) evaluated the ability of aluminum hydroxide ($Al(OH)_3$) to remove phosphorus from synthetically prepared phosphorus solutions and raw wastewater. Synthetically prepared $Al(OH)_3$ (14.3 mg Al/l) and phosphorus solution (2 to 15 mg /l-P) were shaken on an orbital shaker at 150 rpm for 60 minutes and the supernatant was analyzed for phosphorus concentration. Three different types of phosphorus solutions, containing orthophosphate, condensed phosphorus or organic phosphorus, were used in this study. Results showed that at a molar ratio of 8 mol Al/mol P, more than 95% orthophosphate and condensed phosphorus removal and approximately

40% organic phosphorus removal could be achieved. The authors also conducted jar tests using water treatment alum sludge and wastewater. The test suspension was rapid mixed for 5 minutes at 100 rpm, followed by slow mixing for 30 minutes at 30 rpm and then settling for 30 minutes. Results showed that an aluminum to phosphorus ratio of 15.2 mol Al/mol P could achieve more than 85% total phosphorus removal when the wastewater total phosphorus concentration was 2.8 mg-P/l and the initial pH was 7.87. However, these results could not be compared with the results obtained from synthetic solutions because of difference in experimental methods and the type of phosphorus measured. Also, the mechanism of phosphorus removal in those two methods may differ significantly.

Huang and Chiswell (2000) conducted a study on phosphorus removal with spent alum sludge in an adsorption column. The water treatment plant alum sludge used for this study was air-dried, lightly ground and passed through a 2.8 mm diameter sieve. A bench-scale continuous flow system was set up for the experiment and operated for up to 40 hours. For each run, 1 kg of alum sludge solids was packed into the reactor that was then filled with approximately 4 liters of wastewater. The influent flow rate was approximately 10 ml/min and the recycled effluent flow rate was 100 ml/min. The phosphate concentration was analyzed using the flow injection analysis (FIA) method. The effluent samples were injected into the FIA system every 6 minutes. The 10-hour continuous flow study indicated that approximately 55% phosphate removal was achieved after the first 20 minutes and 68% removal after a period of 10 hours. pH varied from 6.5 to 7 during the experimental period.

Kim et al. (2003) determined the phosphorus removal efficiency of water treatment plant alum sludge in aqueous solutions. The water treatment plant alum sludge was air dried and passed through a 2 mm sieve. The investigators conducted batch sorption tests and column tests to determine the phosphorus removal efficiency. In the batch tests, 1 gram of dried alum sludge was mixed with 30 ml of phosphorus solution at initial concentrations of 100, 200, 400, 800, 1000, 2000 and 4000 mg P/l in 0.01M KCl

(solution pH = 7.1). The mixtures were shaken overnight and then centrifuged at 3000 rpm for 10 minutes. The phosphorus concentration of the supernatant was determined with an ICP-AES. A Langmuir isotherm was fit to the batch test results and indicated the maximum adsorption capacity of alum sludge for orthophosphate to be 25 mg-P/g of alum sludge. Adsorption isotherms were plotted for four forms of phosphorus and the order for maximum adsorption capacity was found to be orthophosphate > pyrophosphate > triphosphate > organic phosphate (adenosin). The column (a polyethylene tube, 13 cm in length and 4 cm in diameter) experiment was conducted with 130 grams of air-dried alum sludge and a constant 3 ml/min upward flow of phosphorus solution (initial orthophosphate concentration was 30 mg/l). The column test indicated that alum sludge removed phosphorus to less than 1 mg/l-P over 250 pore volumes at pH 4 and 200 pore volumes at pH 5, respectively.

Georgantas and Grigoropoulou (2005) used spent alum sludge from a water treatment plant to remove phosphorus as orthophosphate from both synthetically prepared wastewater and raw sewage. Jar tests were carried out to facilitate mixing between wastewater and alum sludge. 250 ml of raw wastewater, spiked with different concentrations of alum sludge was stirred at 90 rpm for 3 minutes and then at 40 rpm for 30 minutes followed by 30 minutes of settling. The pH was maintained at 6 and the temperature during the experimental period was 25°C. Synthetic wastewater was prepared by dissolving 50 mg N/l as NH_4Cl and 10 mg P/l as KH_2PO_4 in 100 ml of deionized water to yield an initial phosphorus concentration of 10 mg P/l. The orthophosphate removal efficiency of alum sludge from synthetic wastewater was compared with alum, iron chloride, iron sulfate and calcium hydroxide. Results indicated that alum sludge was less efficient compared to alum, iron chloride and iron sulfate in removing phosphorus from synthetic wastewater. In order to reduce the phosphorus concentration of synthetic wastewater to less than 1 mg/l-P, 75 mg Al/l alum sludge was required whereas only 15 g Al/l of fresh alum was required to achieve a similar removal. In the case of raw wastewater, an alum sludge concentration of 75 mg Al/l (initial orthophosphate concentration 8.3 mg P/l) could remove 60% of the orthophosphate. The lower removal efficiency compared to the synthetic wastewater was attributed to the

presence of other species in the raw wastewater that may have competed with phosphorus for adsorption sites on the applied alum sludge.

2.6 Effect of temperature and pH on phosphorus removal

Several factors can affect the efficiency of phosphorus removal by alum sludge. Among these, pH and temperature have been reported to have the most significant effects.

2.6.1 Effect of temperature

The effect of temperature on adsorption is a very complex phenomenon for which not much information is available in the literature. Benefield et al. (1982) stated that the temperature at which the adsorption process is conducted affects both the rate and the extent of adsorption. Usually the adsorption rate increases with increasing temperature but as adsorption is an exothermic process, the degree of adsorption will increase at low temperature. This statement that adsorption is an exothermic process has been supported by other researchers (Zarzychi and Chacuk, 1993; Ruthven, 1984). Ruthven (1984) also reported that the Langmuir isotherm constants should increase with decreasing temperature. Zarzychi and Chacuk (1993) stated that a rise in temperature induces change in solubility of adsorbent, chemical reaction rates and physiochemical properties of the solid and liquid and thus it affects the adsorption. However, some researchers found that phosphorus adsorption increases with temperature. Ugurlu and Salman (1998) reported that the rise of temperature could affect the solubility and the chemical potential of adsorbent fly ash. These researchers conducted their experiment with 4 g/l of fly ash at temperatures of 27.8, 40 and 50°C and found that the reaction rate increased with increasing temperature up to 40°C but decreased at 50°C. They explained that after a certain temperature, desorption might become predominant. They also reported that temperature had no significant effect on the change in adsorption capacity when the initial phosphate concentration was very low (20 mg/l-P) and the adsorbent quantity was 4 g/l. They concluded that phosphorus removal by adsorption onto fly ash surface increased as a function of phosphorus concentration in the solute at any temperature.

Mohanty et al. (2004) investigated the effect of temperature on the removal of phosphorus from aqueous solution using 2 g/l alumized red mud within a temperature range of 40°C to 80°C at pH 4.5. Their results indicated that although the percent adsorption increased slightly up to a particular temperature, it decreased sharply from 85% (at 70°C) to 50% (at 80°C) at higher temperatures (initial phosphorus concentration 10 mg/l-P). This sharp decrease in adsorption was attributed to the tendency of the molecules to escape from the interface at higher temperatures. Unnithan et al. (2001) found the adsorption process to be an endothermic process. They performed adsorption tests for phosphate removal using iron (III) loaded carboxylated polyacrylamide grafted sawdust at 30, 40, 50 and 60°C. These investigators reported that Langmuir constants q_{max} and b increased with increasing temperature. They also indicated that the extent of adsorption significantly increased with the initial concentration of phosphate, because, at high initial concentration the ratio of initial number of moles of phosphorus to the available adsorption sites is high, so the fractional adsorption becomes dependent on initial concentration.

2.6.2 Effect of pH

The pH of the solution is an important factor in the adsorption process and it governs the extent of adsorption of anions at the adsorbent and adsorbate interface. Several researchers tried to evaluate the pH effect on phosphorus adsorption. Kim et al., (2003) stated that pH dependence of phosphate adsorption to alum sludge is due to the solubility of Al and the surface charge of aluminum hydroxide at different solution pH values. Their column test results indicated that the capacity of alum sludge to remove phosphorus from aqueous solutions increased with decreasing initial solution pH (the pH varied from pH 3 to 12). At an initial pH of 3, the effluent orthophosphate concentration was below 1 mg/l when the orthophosphate concentration of the synthetic influent solution was 30 mg/l. Altundogan et al. (2001) reported that in the removal of phosphorus from aqueous solution using bauxite adsorption was higher in acidic solution. The highest percent orthophosphate adsorption was found using 10 g/dm^3 bauxite at a final solution pH of 4.45 when the initial orthophosphate concentration was 10 mg P/dm^3 at 25°C. They

explained that the predominant orthophosphate species was the $H_2PO_4^-$ ion in final pH 4.45 and the point of zero net proton charge (PZNPC) value of bauxite used in this study was found to be at 8.39, below which the surface is positively charged. Thus, the positively charged groups on the adsorbent surface may adsorb the dominant phosphate species of $H_2PO_4^-$. Mohanty et al. (2004) also evaluated the pH effect (pH 3 to 6) on the adsorption of phosphorus from aqueous solutions with alumized red mud. They found that the maximum phosphorus adsorption was achieved at pH 4.5 using 2 g/l of alumized red mud and an initial phosphorus concentration of 20 mg P/l. At pH values greater than 4.5, phosphorus removal decreased sharply because of the stronger competition from the hydroxide ions on the adsorbent surface.

The solubility of aluminum is highly dependent on pH and this determines the amount of aluminum present in the solid phase, which in turn affects the adsorption phenomenon (Galarneau and Gehr, 1997). At low pH, positively charged, soluble hydrolysis products and the aquo-metal ion (Al^{3+}) is formed. Whereas at high pH, the negatively charged soluble hydrolysis product ($Al(OH)_4^-$) is formed. In Al protolysis it has been found that $Al(OH)_3$ is the predominant form at pH range 4.5 to 8 for moderate concentration (10^{-5} to 10^{-3}M). Above pH 8 $Al(OH)_4^-$ is the predominant form (Gates, 1991). The minimum solubility pH of aluminum hydroxide at 25°C is approximately 6.3 and at 4°C the minimum solubility is reached at pH 6.8 (AWWA, 1999). The pH at which the surface is neutral is a characteristic of a solid and is referred to as the point of zero charge (PZC). The PZC of $Al(OH)_3$ is at pH 5 (Benjamin, 2002). In wastewater at pH below the point of zero charge of $Al(OH)_3$ the positively charged Al polyhydroxide predominates.

In the aqueous solutions various types of protonated phosphate species are formed, depending on pH. The presence of different forms of phosphorus in solution also depends on the solution pH. In domestic sewage, the most dominant forms of orthophosphate in the pH range from 6.5 to 8 are $H_2PO_4^-$ and HPO_4^{2-} (Snoeyink and Jenkins, 1980). For condensed phosphorus in this pH range (approximately pH 6.5 to 8) normally $HP_3O_{10}^{4-}$ and $HP_2O_7^{3-}$ are found to be predominant (Gates, 1991).

Adsorption is not the only process responsible for phosphorus removal. Sometimes precipitation may have a very significant role in phosphorus removal. For some anions, a transition from an adsorbed state to formation of a surface precipitate is possible ($AlPO_4$); however the sorption density of many of these ions seems to reach an upper limit imposed by availability of sites and/or build up of negative surface charge, reducing the likelihood that the ions will form surface precipitates with the metal ion of the adsorbent phase (Benjamin, 2002). Lee et al. (1997) indicated that the predominant removal mechanism for phosphorus from soil media was sorption at pH levels less than 8 and precipitation at pH levels greater than 10.

2.7 Need for the research

This research was conducted to find an alternate disposal option for water treatment plant alum sludge by evaluating the phosphorus removal efficiency of alum sludge from raw sewage. Past study findings regarding phosphorus removal using alum sludge were very encouraging because the researchers observed good phosphorus removal. But most of the studies were conducted using synthetically prepared alum sludge or wastewater and the results might be different when using actual wastewater samples. So, in this study alum sludge was collected from Rossdale water treatment plant and the raw sewage was collected from Gold Bar wastewater treatment plant to represent realistic conditions.

The effect of temperature and pH might be very important factors on phosphorus adsorption. The effect of temperature on phosphorus adsorption observed by other researchers was contrasting and no specific research work was conducted to understand the temperature effect on phosphorus removal using alum sludge. In many studies researchers tried to understand the pH effect on phosphorus adsorption. Among them, Kim et al. (2004) conducted a phosphorus removal study using alum sludge and evaluated the pH effect within the range of 3 to 6. The current study evaluates the temperature effect (5 to 19°C) and pH (6.5 to 8) effect on phosphorus removal using waste alum sludge and raw municipal wastewater to represent WWTP and WTP conditions.

The extent of the desorption of adsorbed phosphorus on alum sludge was also investigated briefly. Altundogan et al. (2001) tried to understand the desorption property of orthophosphate which was prevoiulsly adsorbed onto bauxite, but no studies have tried to evaluate the desorption properties of the adsorbed phosphorus from alum sludge. In this study an attempt was made to understand the mobility of the adsorbed phosphorus by desorption test at two different pH levels which might be encountered during sludge treatment and disposal.

3 METHODOLOGY

This chapter details the materials and methods used in this study. Raw samples characteristics, metal concentration, isotherm test, evaluation of pH affect and desorption test methods and procedures are described in this chapter.

3.1 Samples

Samples were obtained from the Rossdale Water Treatment Plant and the Gold Bar Wastewater Treatment Plant on August 8, 23, 30, and September 6, 2005. Grab samples of raw wastewater were collected from the head works of the Gold Bar WWTP on all these days except on August 8, when a 24-hour composite sample of raw wastewater was collected. Rossdale WTP clarifier blowdown was collected from Clarifier C 2-1 as grab samples.

3.2 Methods and procedures

Analyses were done either at the Gold Bar wastewater treatment plant laboratory or at the University of Alberta. The pH, alkalinity and orthophosphate analyses were performed in the University of Alberta laboratory, while total solids, total suspended solids, total aluminum, dissolved aluminum, and total phosphorus were measured at the GBWWTP laboratory. Clarifier blowdown and raw wastewater samples were analyzed on the day of collection. The total phosphorus and orthophosphate in samples from adsorption tests were either analyzed on the day of the test, or the samples were preserved by acidification and stored at 4°C for analysis on the following day.

3.2.1 Raw Sample Characteristics

Each sample of raw wastewater and clarifier sludge was subjected to the following analyses: pH, alkalinity, total solids (TS), total suspended solids (TSS), orthophosphate and total phosphorus.

The pH was measured according to Method 4500-H^+ B, Electrometric method (APHA et al., 1998) using a Fisher Scientific AR 15 pH meter.

Total alkalinity as mg/l $CaCO_3$ (to pH 4.5) of raw sewage and alum sludge were measured according to Method 2320 B, Titration method (APHA et al., 1998).

Total solids tests for both alum sludge and raw sewage were performed according to Method 2540 B, Total Solids dried at 103 - 105°C method (APHA et al., 1998).

Total suspended solids of both alum sludge and raw sewage were measured according to Method 2540 D, Total Suspended Solids dried at 103 - 105° C method (APHA et al., 1998). Method detection limit is 0.8 mg/l.

Orthophosphate as mg/l-P and total phosphorus as mg/l-P were measured for both raw sewage and alum sludge after sampling. The method used for measuring orthophosphate concentration was the PhosVer 3 (Ascorbic acid) method, which was the HACH Method 8048 (HACH, 1997). Two standard curves, absorbance verses concentration curves, were developed with PhosVer 3 phosphate reagent pillows within phosphorus concentration of 0 – 1.25 mg/l-P and 0 to 1 mg/l-P (see Appendix A, Figure A-1 and Figure A-2). The samples collected on August 8 were analyzed using standard curve A shown in Figure A-1 and the rest of the samples were analyzed using a standard curve B shown in Figure A-2. The absorbance was measured at 890 nm using an Ultrospec 2000 UV/Visible spectrophotometer.

The method used for total phosphorus analysis was the Standard Method 4500-P F: Method Code 582, Automated Block Digestion, Ascorbic acid, Molybdenum Blue Colorimetric method (APHA et al., 1998). Method detection limit is 0.01 mg/l.

Total aluminum and dissolved aluminum concentrations were determined according to Standard Method 3120 B, Inductively Coupled Plasma (ICP) method (APHA et al., 1998). The method detection limit was 0.007 mg/l. These measurements were performed in triplicate.

All glassware was acid washed prior to use. Each analysis was done in triplicate and averaged results were used for the analysis of experimental results.

3.2.2 Isotherm testing for orthophosphate and total phosphorus adsorption

Equilibrium adsorption tests were performed at 5, 12 and 19°C without altering the initial pH of the test mixtures. Each set of experiments was performed separately with freshly collected raw sewage and alum sludge. Mixtures of alum sludge and raw wastewater were made on a volume basis in 250 ml Erlenmeyer flasks. Ratios of alum sludge to raw sewage were chosen to yield a range of phosphorus adsorptions suitable for plotting an isotherm for each temperature tested.

At temperatures of 19°C, 12°C and 5°C the total aluminum concentration varied from 2.7 to 43 mg/l, 5.5 to 109 mg/l and 4.4 to 70 mg/l in dilutions respectively (the volumetric ratio alum sludge: raw sewage were 1:79 to 1:4, 1:399 to 1:19 and 1:79 to 1:4 respectively). Each set of equilibrium tests was conducted in a temperature controlled room. Test flasks were shaken on an Innova 2100 platform shaker at 150 rpm for 15 hours. At the end of each test, flask contents were allowed to settle for 90 minutes before supernatant was decanted and analyzed for orthophosphate and total phosphorus. Each test was performed in triplicate, while each sample was analyzed in duplicate.

3.2.3 Effect of pH on orthophosphate and total phosphorus removal

The effect of pH on phosphate adsorption was assessed by conducting a set of equilibrium tests at pH 6.5, 7 and 8 at room temperature, 19°C. These levels were

selected because typically the pH of both the alum sludge and raw sewage was near to or slightly higher than neutral (pH 7). The effect of pH was observed using an alum sludge to raw sewage volumetric ratio of 1:19, with a total aluminum concentration of 9.2 mg/l. This dilution ratio was chosen because previous trials using this ratio resulted in a moderate phosphorus removal at a pH value close to neutral. The desired mixture ratio of alum sludge and raw wastewater was first prepared in a 250 ml Erlenmeyer flask. This resulted in a pH of from 7.7 to 7.8. The mixture's pH was then adjusted initially to the desired value using 1.5M NaOH or 1.5M HCl. The equilibrium testing and supernatant analyses were conducted as indicated above.

3.2.4 Desorption testing

The purpose of this set of tests was to determine the mobility of the adsorbed phosphorus. Settled sludge from the equilibrium tests (pH was 7.5) was filtered through a Whatman glass fiber filter (size 4.7 cm), dried at 103°C and weighed. The dried sludge was mixed with 200 ml deionized (DI) water that had been adjusted earlier to pH 5 or pH 9. These pH values were selected in order to simulate the extremes of acidic and basic conditions that the sludge might be expected to experience during sludge handling and disposal. The pH was adjusted using either 0.15M NaOH or 0.15M HCl solution. The mixtures were shaken on an Innova 2100, platform shaker at 150 rpm for 91 hours and 30 minutes and then allowed to settle for 90 minutes. This test was conducted at room temperature (19°C). After shaking, the supernatant was collected and the orthophosphate and total phosphorus content were measured. Because only a small amount of alum sludge sample was available from the equilibrium adsorption tests, no duplication of the mobility test was performed.

4 RESULTS AND DISCUSSION

This chapter presents the experimental results obtained in this study, and a discussion of the results. This chapter is subdivided into four parts: characteristics of alum sludge and raw sewage, temperature effect and pH effect on phosphorus removal and the desorption test.

4.1 Characteristics of alum sludge and raw sewage

The raw wastewater and alum sludge were collected on the day of each experimental run. Each sample was analyzed to determine its pH, alkalinity, TS, TSS, orthophosphate and total phosphorus concentrations. The results showed wide ranges of variation, which is expected as the characteristics of the samples are affected by the weather conditions, eg. rainfall affects the turbidity of the raw water and that could effect the total solid concentrations of alum sludge. The ranges of parameter values for the alum sludge and raw wastewater samples are shown in Table 4—1 and Table 4—2, respectively. Data from all the analyses are shown in Tables B-1 to B-11 (see Appendix B).

Table 4—1. Alum sludge characterization summary.

Parameter	Units	Value
pH		7.1 to 7.3
Alkalinity	mg/l as $CaCO_3$	125 to 173
TS	mg/l	1,719 to 23,643
TSS	mg/l	1,330 to 23,267
Orthophosphate	mg/l – P	0 to 0.01
Total Phosphorus	mg/l – P	0.1 to 12.1
Total Aluminum	mg/l	184 to 2183
Dissolved aluminum	mg/l	0.26 to 0.46

All of the parameter values listed in Table 4—1 are within the ranges of parameter values reported by the UMA group (1984), which conducted a survey of alum sludge produced in Alberta water treatment plants (see Table 2-3).

During the experimental period, the pH of alum sludge (7.1 to 7.3) was found to be slightly above the neutral point and within the typical pH range from 5.5 to 7.5. There was little information available in the literature regarding typical alkalinity values for waste alum sludge. The TS range measured in the current study (approximately 0.8 to 2.3%) is in agreement with the typical range cited by UMA (1984) and shown in Table 2-3. According to the UMA group report, suspended solids in waste alum sludge typically represent between 75 to 99% of TS. From the current study, except for the first alum sludge sample, the TSS ranged from 77 to 98% of TS (see Appendix B, Table B-5) which agrees well with the reported typical range. Although, the lowest total phosphorus concentration during the experimental period fell outside the lowest expected concentration of 0.3 mg/l as reported by the UMA group, the upper limit was well within the typical range of 0.3 to 200 mg P/l. According to the UMA group (1984), the aluminum contents for the alum sludge is typically between 4 to 11% of the total solids of alum sludge. The total aluminum concentration in terms of total solids measured during the current study was 3.9 to 10.7%, which matches well the expected range. However, the aluminum concentration range reported by Huang et al. (2000) was from 1300 to 5600 mg/l which is significantly different from the range observed here. This difference may be due to the type of raw water treated and the concentration of alum used for coagulation.

Table 4—2. Raw sewage characterization summary

Parameter	Units	Value
pH		7.5 to 7.7
Alkalinity	mg/l as $CaCO_3$	342 to 439
TS	mg/l	576 to 1134
TSS	mg/l	141 to 336
Orthophosphate	mg/l – P	4.9 to 9.4
Total Phosphorus	mg/l – P	10 to 15
Total aluminum	mg/l	1.14 to 1.31
Dissolved aluminum	mg/l	0.24 to 0.29

Similarly, the ranges of parameter values shown in Table 4—2 are in agreement with typical parameter values for an untreated domestic wastewater reported in Metcalf and Eddy (2003) (see Table 2-2). Total solid (TS) and total suspended solid (TSS) concentrations range of Gold Bar raw sewage fell in the untreated domestic wastewater TS and TSS range of 390 to 1230 mg/l and 120 to 400 mg/l respectively. The total phosphorus concentration range is also comparable with the typical range of 4 to 16 mg/l-P. As aluminum content of the raw wastewater in not of serious concern, no expected limit was found in literature for total and dissolved aluminum in the raw sewage. However, the range that was determined during the current study shows that the total aluminum concentration (1.14 to 1.31 mg/l) and dissolved aluminum concentration (0.24 to 0.29 mg/l) for raw wastewater is not very high, which was expected.

4.2 Temperature effects on phosphorus removal

A series of 15-hour adsorption tests was conducted at 5°C, 12°C and 19°C. The results are presented in graphical form in Figures 4-1 to 4-6 for both orthophosphate and total phosphorus. Each figure represents the percent phosphorus removal and the extent of phosphorus adsorption per g total Al in the applied alum sludge. From all the figures it is quite obvious that phosphorus removal increased with increasing mass of total aluminum present in the mixture. On the other hand, the trend of decreasing unit adsorption of phosphorus with increasing mass of total aluminum present is quite the opposite. This can be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process and hence phosphorus adsorption does not increase proportionately with the increase in total amount of aluminum. Since the percent removal is dependent on the total available sites, it increases with the increase in aluminum concentration. Similar trends were observed for both orthophosphate and total phosphorus adsorption. From Figures 4-1 to 4-6, it can be also observed that alum sludge has lower removal efficiency of total phosphorus compared to orthophosphate. As mentioned in the literature review chapter, the orthophosphate removal is always higher than the condensed and organic phosphate removal (Kim et al., 2003). Therefore, in case of total phosphorus, slightly lower removal is expected.

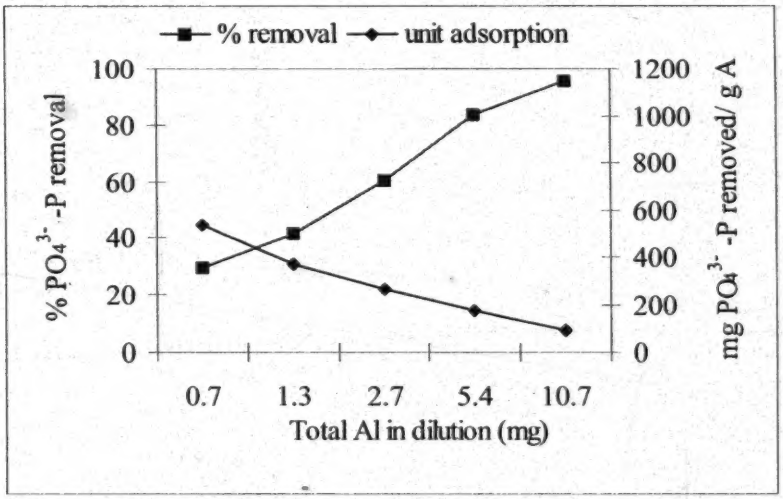


Figure 4-1. Orthophosphate removal from raw sewage at 19°C.

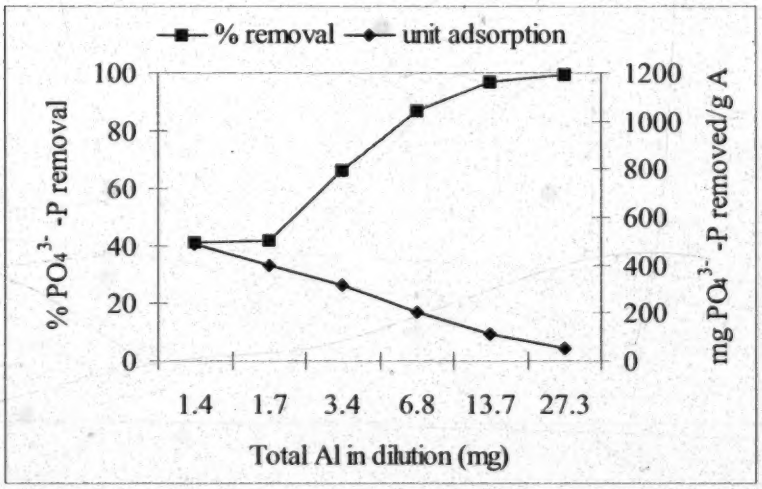


Figure 4-2. Orthophosphate removal from raw sewage at 12°C.

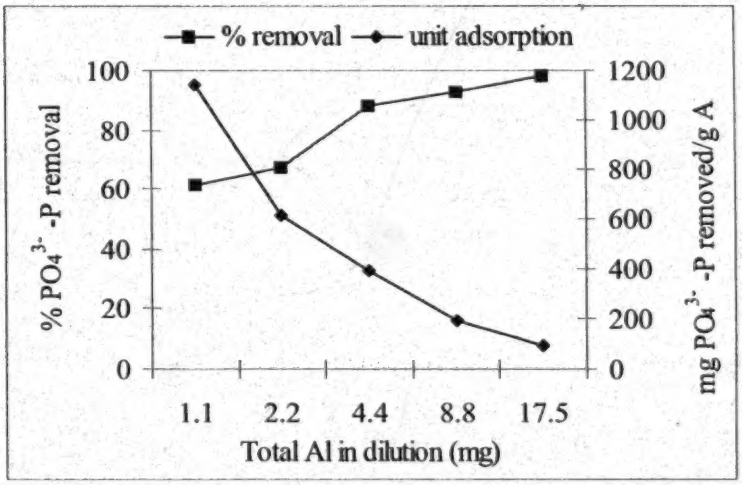


Figure 4-3. Orthophosphate removal from raw sewage at 5°C.

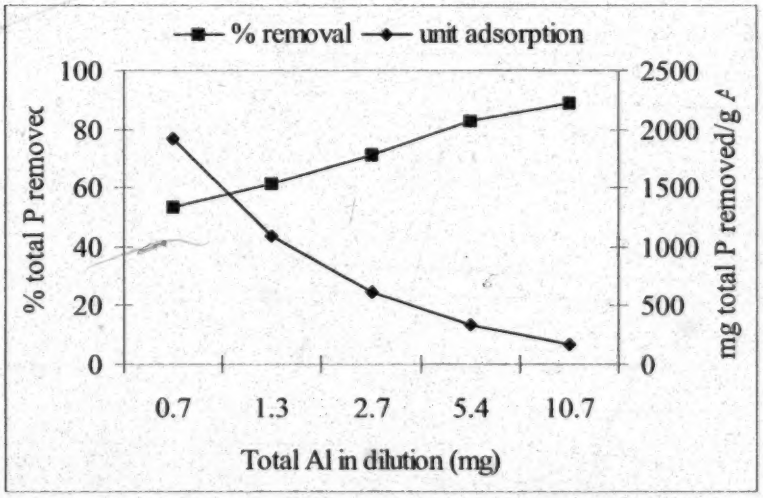


Figure 4-4. Total phosphorus removal from raw sewage at 19°C.

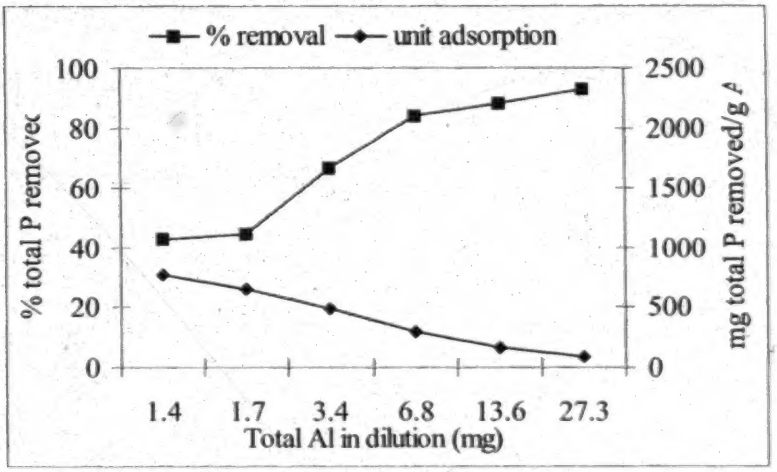


Figure 4-5. Total phosphorus removal from raw sewage at 12°C.

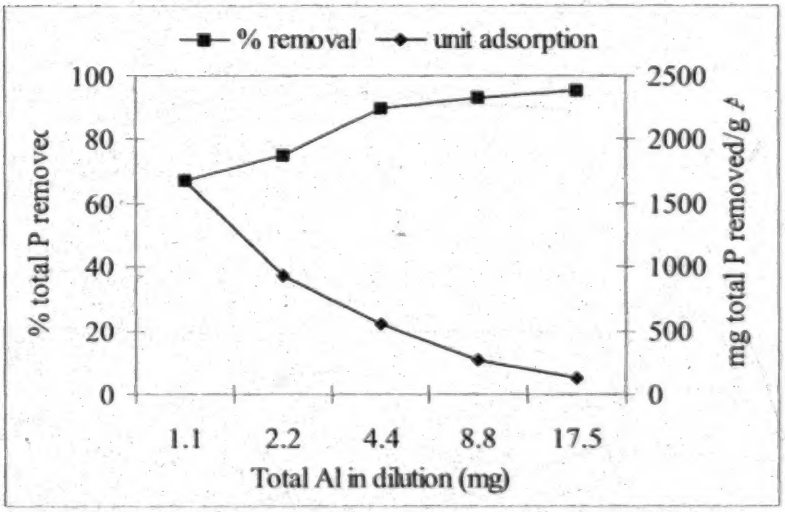


Figure 4-6. Total phosphorus removal from raw sewage at 5°C.

Table 4-3 compares the total phosphorus and orthophosphate removal reported in different studies at room temperature. A brief description of the experimental conditions of those studies is also provided in the table.

Table 4—3. Percent phosphorus removal by alum sludge at room temperature reported in different studies.

Type of phosphorus	Initial phosphorus (mg P/l)	Alum sludge (mg Al/l)	Experimental condition	Percent removal	Reference
Orthophosphate	10.47	32.6	pH 8.08, jar test	75	Barr A. (1992)
Orthophosphate	8.3	75	pH 6, jar test	60	Giorgantas et al. (2005)
Orthophosphate	3.9	42.8	pH 7.5, isotherm test	95.9	This study
Total P	2.8	36	pH 7.87, jar test	85.7	Galarneau et al. (1996)
Total P	10.8	75	pH 6, jar test	65	Giorgantas et al. (2005)
Total P	7.77	42.8	pH 7.5, isotherm test	88.8	This study

The orthophosphate and total phosphorus removal in this study was conducted through isotherm test whereas Barr (1992), Galarneau et al. (1996) and Giorgantas et al. (2005) conducted their experiment in jar test apparatus. Even the initial phosphorus concentration varied for different studies. However, the phosphorus removal efficiency of alum sludge in all those studies was greater than 60% regardless of the experimental condition adopted.

The experimental data of adsorption density (mg phosphorus removed/g Al_T) and equilibrium concentration of phosphorus present in dilution (see Appendix C, Tables C-2, C-3, C-5, C-6, C-8 and C-9) were used to calibrate the Freundlich and Langmuir isotherm expressions. The calibration indicated that the data fit the Freundlich isotherm better than the Langmuir isotherm (results shown in Appendix C, Tables C-10 to C-11). Data analysis was conducted using the solver tool in Microsoft Excel. The Freundlich isotherms for adsorption of orthophosphate and total phosphorus at 19°C, 12°C, and 5°C are shown in Figures 4-7 to 4-12.

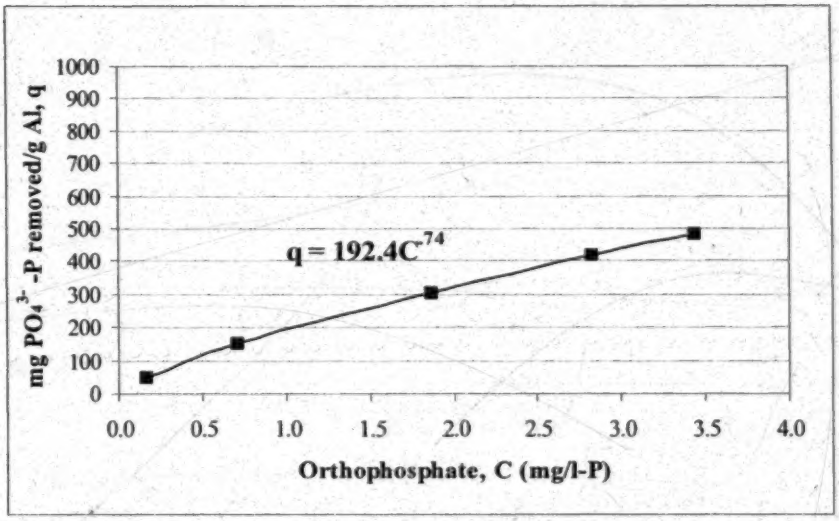


Figure 4-7. Freundlich isotherm for orthophosphate adsorption on aluminum at 19°C.

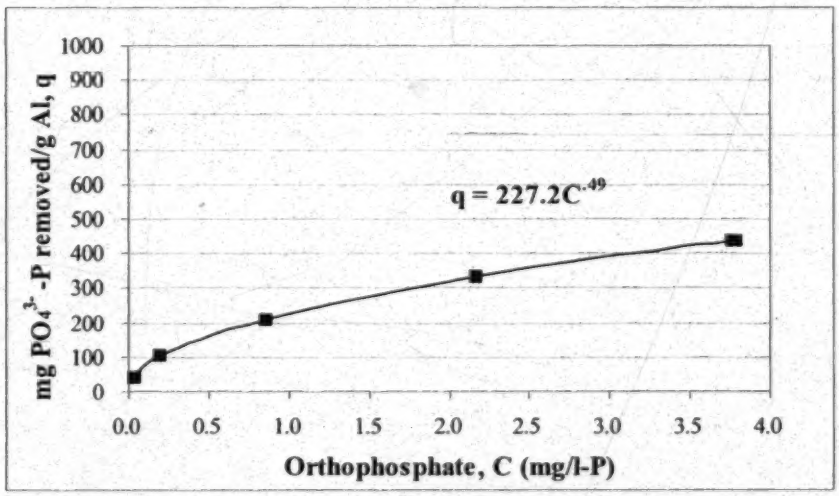


Figure 4-8. Freundlich isotherm for orthophosphate adsorption on aluminum at 12°C.

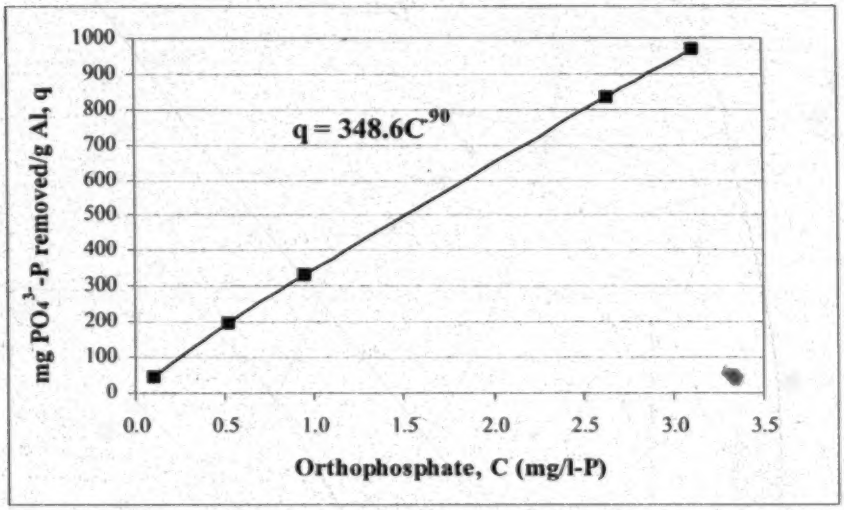


Figure 4-9. Freundlich isotherm for orthophosphate adsorption on aluminum at 5°C.

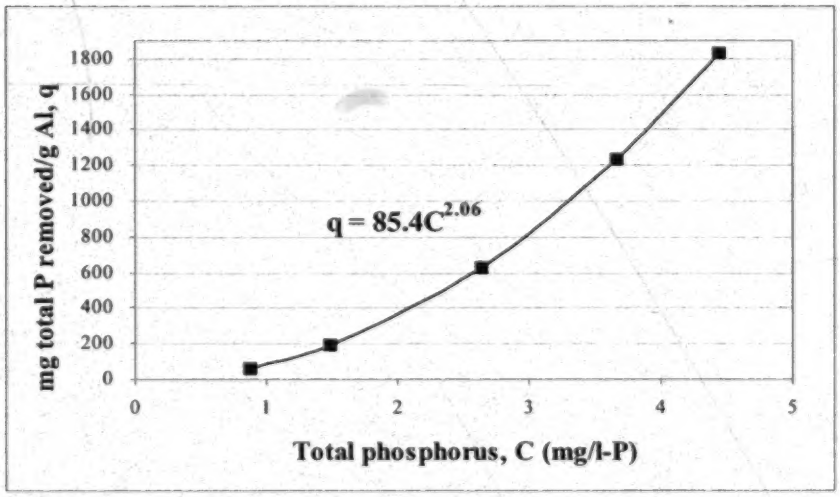


Figure 4-10. Freundlich isotherm for total phosphorus adsorption on aluminum at 19°C.

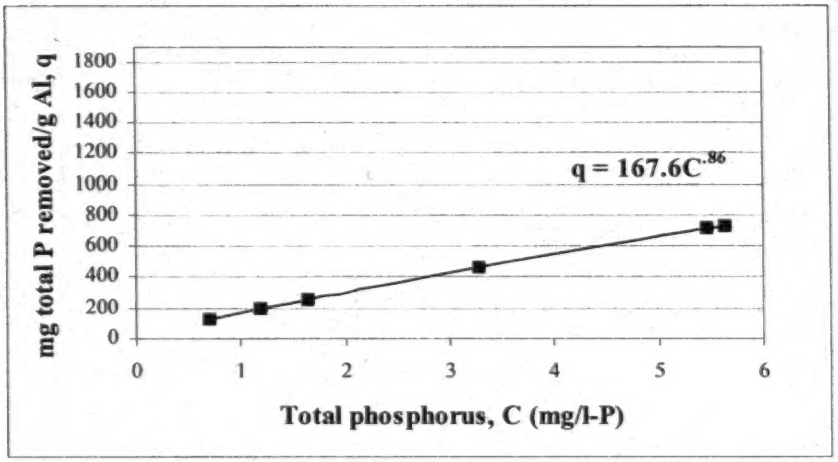


Figure 4-11. Freundlich isotherm for total phosphorus adsorption on aluminum at 12°C.

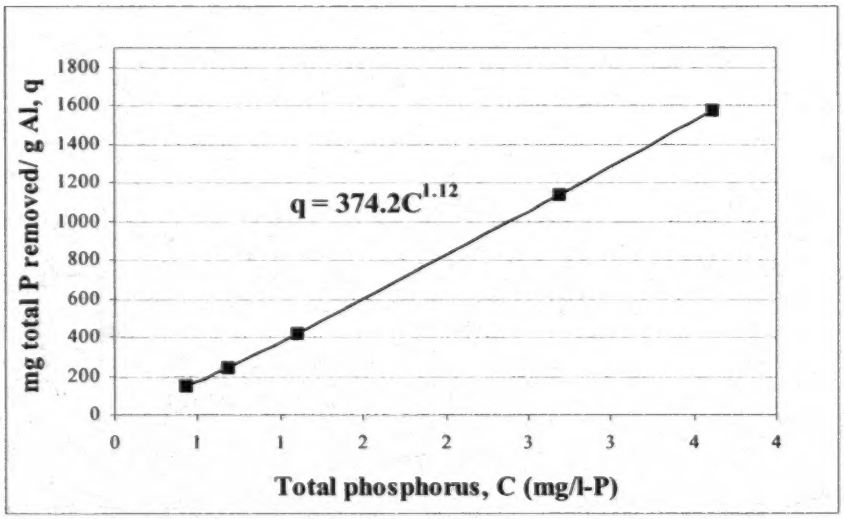


Figure 4-12. Freundlich isotherm for total phosphorus adsorption on aluminum at 5°C.

The Freundlich isotherm expression contains two constants: K, which is the measure of capacity of the adsorbent (mass adsorbate/mass adsorbent) and 1/n, which is the measure of the strength of adsorption. For constant values of equilibrium concentration and 1/n,

the larger the value of K, the larger the adsorption capacity is. Similarly, for fixed values of equilibrium concentration and K, a larger value of 1/n indicates a stronger adsorption bond. The estimated values of the Freundlich isotherm parameters for the temperatures tested are shown in Tables 4-4 and 4-5. Although the trend is not entirely clear, it appears that adsorption capacity (as characterized by Freundlich parameter values, K) increases with decreasing temperature. As adsorption has been reported to be an exothermic process (Zarzychi and Chacuk, 1993, Ruthven, 1984 and Benefield et al.1982), this trend is quite predictable. In case of orthophosphate and total phosphorus the trend for 1/n values are not conclusive.

Table 4—4. Freundlich isotherm parameter values for orthophosphate adsorption in terms of total aluminum at 5, 12, and 19°C.

Temperature	Freundlich isotherm, $q = KC^{1/n}$		
	1/n	K (l/g Al_T)	R^2
19° C	0.74	192.4	0.93
12° C	0.49	227.2	0.96
5° C	0.90	348.6	0.88

Table 4—5. Freundlich isotherm parameter values for total phosphorus adsorption in terms of total aluminum at 5, 12, and 19°C.

Temperature	Freundlich isotherm, $q = KC^{1/n}$		
	1/n	K (l/g Al_T)	R^2
19° C	2.06	85.4	0.97
12° C	0.86	167.6	0.97
5° C	1.12	374.2	0.96

4.3 pH effects on phosphorus removal

Because of its effect on the solubility of the adsorbate (and in this case on the solubility of adsorbent as well) and on the surface characteristics of an adsorbent, pH is one of the main factors that can affect adsorption. Therefore, the adsorption of phosphorus by alum sludge was studied at pH 6.5, 7 and 8. These levels were selected to encompass the values expected in practice if alum sludge were mixed with raw wastewater. The mass of total aluminum selected for the test mixture had resulted in a moderate degree of phosphorus removal at room temperature during the previous trial. The results of this set of tests for orthophosphate and total phosphorus are shown in Figure 4-13 and 4-14. The detailed results are provided in Appendix D (Tables D-1 to D-3).

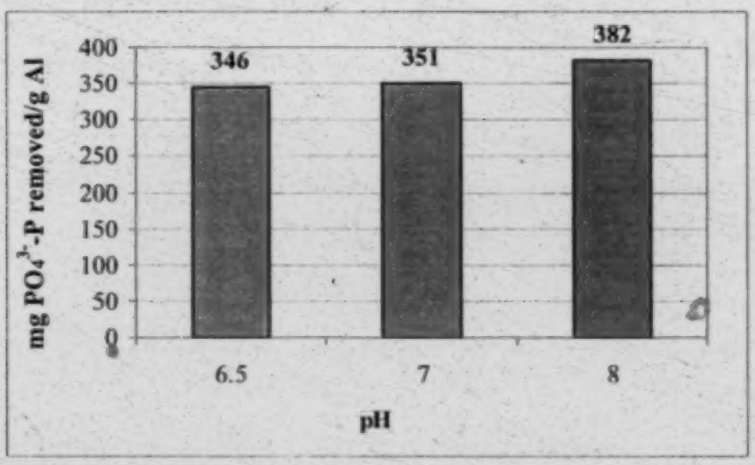


Figure 4-13. Effect of pH on orthophosphate adsorption.

Figure 4-13 shows a trend of slightly increasing removal of orthophosphate with increasing pH. An analysis of variance (ANOVA) was performed in order to determine whether there was any significant difference in orthophosphate removal at the different pH levels. The ANOVA results (shown in Appendix D, Tables D-4) indicate that there is no significant difference between the orthophosphate removals at the three pH levels ($p = 0.33$). This finding is inconsistent with the previous research studies. Kim et al. (2003) found a sharp decreasing trend for orthophosphate adsorption at pH greater than 7. However, they used water treatment plant alum sludge for phosphorus removal in

aqueous solutions whereas this study used raw sewage and the difference in samples and experimental conditions could lead to the different findings.

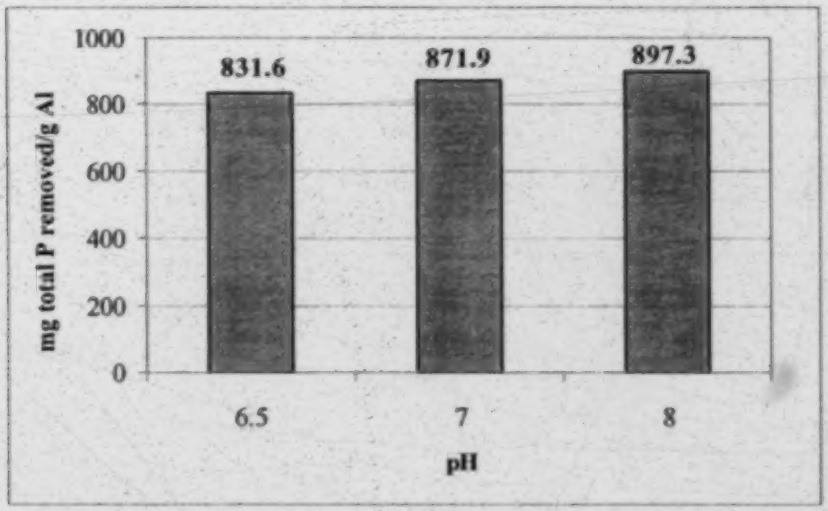


Figure 4-14. Effect of pH on total phosphorus adsorption.

Adsorption test results for of total phosphorus are shown in Figure 4-14. There appears to be a trend an increasing of phosphorus removal with the increase in pH, and an ANOVA (Appendix D, Table D-5) confirms that there was a significant difference between the mean total phosphorus removals ($p = 0.002$) at different pH levels. Total phosphorus comprises several different forms of phosphorus. Therefore, it is not inconceivable that non-orthophosphate forms of phosphorus will respond differently to a change in pH (Altundogan et al., 2001). Additionally, these results suggest that precipitation of orthophosphate by aluminum re-dissolved at the higher pH is not a significant mechanism contributing to phosphorus removal. In Al protolysis at pH values from 4.5 to 8, the predominant form is $Al(OH)_3$ for a moderate Al concentration of 10^{-5} to 10^{-3}M. At pH>8 the predominate form is $Al(OH)_4^-$. In this study, the pH of the solution ranged from 6.5 to 8 and the aluminum concentration of alum sludge was 3.4×10^{-4}M. This suggests that the predominant form of aluminum was solid $Al(OH)_3$ and hence the

mechanism of phosphorus removal by alum sludge was presumably adsorption. Up until now, no studies attempted to observe the effect of pH on phosphorus removal efficiency from raw wastewater by alum sludge.

4.4 Desorption tests

Desorption tests were performed on alum sludge to estimate the mobility of the adsorbed phosphorus during sludge treatment and final disposal. These tests were conducted using alum sludge collected from the adsorption tests (the pH of the adsorption test was 7.5) that was filtered and dried before being placed in pH adjusted deionized water. The tests were performed at 19°C and pH values of 5 and 9 in order to span the anticipated pH range that may be encountered during sludge treatment and disposal. Figure 4-15 shows the mass of orthophosphate released into solution per gram of total aluminum plotted against the mass of orthophosphate that had been adsorbed (during the equilibrium adsorption tests) per gram of total aluminum (see Appendix E, Tables E-1 to E-4).

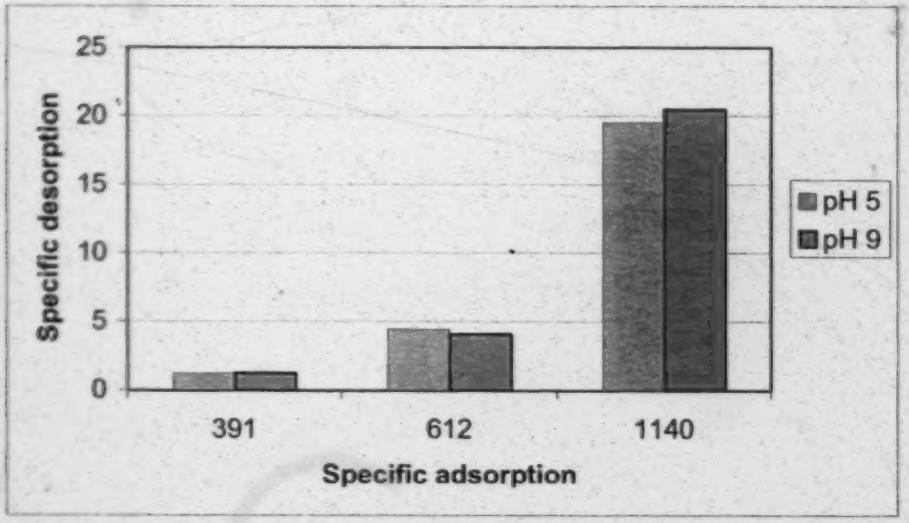


Figure 4-15. Specific masses of orthophosphate adsorbed at pH 7.5 and desorbed at pH 5 and 9 at 19°C. Units: mg P/g total aluminum.

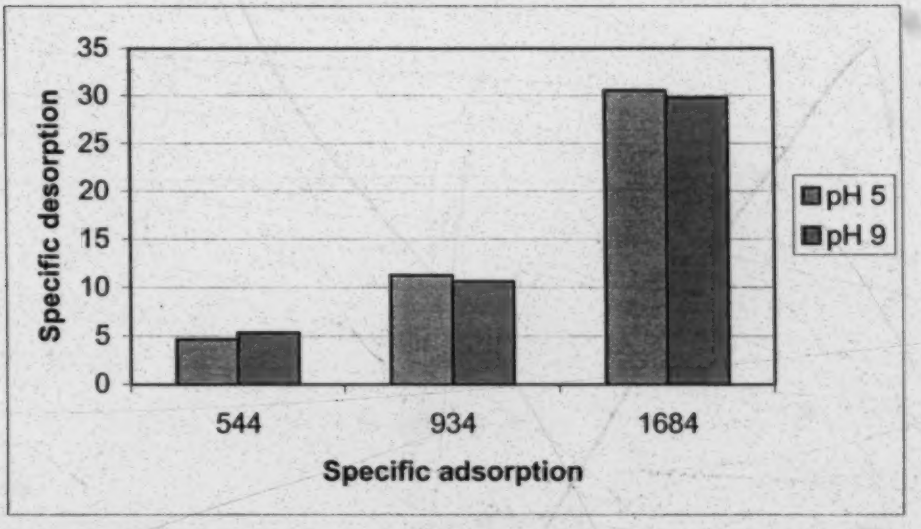


Figure 4-16. Specific masses of total phosphorus adsorbed at pH 7.5 and desorbed at pH 5 and 9 at 19°C. Units: mg P/g total aluminum.

ANOVA analysis (shown in Appendix E, Table E-5) indicated that desorption of orthophosphate was not affected by the solution pH within the range tested ($p = 0.65$). However, desorption increased significantly ($p = 0.001$) with increasing mass of alum sludge. Figure 4-15 shows that the mass released to solution was related to the mass that had been adsorbed per unit mass of total aluminum during the equilibrium adsorption tests. The specific mass of orthophosphate released to solution (per g of total aluminum) ranged from 0.3% to 1.8% of the mass adsorbed (detail calculation shown in Appendix E, Table E-1). The less amount of phosphorus desorption might indicate the mechanism involved for phosphorus adsorption might not be physical adsorption. It may be chemical or ion exchange adsorption. So, more investigations are needed regarding this issue.

Similar results were obtained with respect to total phosphorus released to the solution, as shown in Figure 4-16, with total phosphorus releases ranging from 0.9% to 1.8% (Appendix E, Table E-5). The ANOVA results for total phosphorus was similar to the orthophosphate desorption (shown in Appendix E, Table E-6), showing no significant pH effect on desorption at pH level 5 and 9 ($p = 0.72$).

According to Altundogan et al. (2001) the effects of pH on desorption should be opposite to the pH effect during adsorption. These investigators reported that desorption of orthophosphate from orthophosphate-adsorbed bauxite samples (0.65 mg-P/g bauxite) was lowest (4.7%) at pH 4.45 where previous adsorption test found highest adsorption (67.3%) at this pH level. The percent orthophosphate desorption in solution varied from around 4.8 to 28.7 at pH 5 and 9, respectively. However, in this study no significant variation in desorption was observed (evaluated by ANOVA) between pH 5 and 9 for phosphorus adsorbed at pH 7.5. This may be due to the insignificant and modest effects of pH on the adsorption of orthophosphate and total phosphorus, respectively, observed within the pH range of 6.5 to 8 in the current study. So, the desorption results could not come up with a definite conclusion. More studies are required in this area.

5 CONCLUSIONS AND RECOMMENDATIONS

This study evaluated the ability of waste alum sludge to remove phosphorus from raw wastewater, as a means of estimating the value of discharging waste alum sludge from a water treatment plant to a municipal wastewater treatment plant to assist in phosphorus removal. Alum sludge collected from the Rossdale water treatment plant was mixed with raw wastewater collected from the Gold Bar WWTP at different dilutions and the supernatant was analyzed for orthophosphate and total phosphorus. This study also investigated the effect of temperature and pH on phosphorus removal from raw wastewater by alum sludge. In addition, the mobility of adsorbed phosphorus was tested in order to evaluate the tendency of alum sludge to release the adsorbed phosphorus to the environment when the pH changes. The major findings of this study are as follows.

- The percent removals of orthophosphate were superior to those of total phosphorus.
- The Freundlich isotherm fit the data better than did the Langmuir isotherm. The Freundlich isotherm parameter, K ranged from 192.4 to 348.6 (l/g Al_T) and decreased with increasing temperature for orthophosphate removal, suggesting more efficient orthophosphate removal at lower temperatures. Also, within the temperature range 5 to 19°C, K varied from 85.4 to 374.2 (l/ g Al_T) for total phosphorus removal with the indication of decreasing trend with the increase in temperature. The value of parameter 1/n did not show any trend with the change in temperature, indicating that the strength of adsorption was not affected by temperature for both orthophosphate and total phosphorus.
- The difference in orthophosphate removal at initially adjusted pH levels 6.5, 7 and 8 was not significant at the 95% confidence level ($p = 0.33$). In contrast, total phosphorus removal was significantly affected by pH at the 95% confidence level ($p = 0.002$). The trend observed for total phosphorus removal was a slight increase with increasing pH.
- Desorption testing indicated that adsorbed phosphorus was not very mobile, with desorption of orthophosphate (adsorbed at pH 7.5) ranging from 0.3 to 1.8% at

both pH 5 and 9 and at room temperature (19°C). Desorption of total phosphorus ranged from 0.9 to 1.8% at both pH 5 and 9. There was no significant difference in desorption of any form of phosphorus at pH 5 or 9 (at the 95% confidence level).

Recommendations

This study provides an insight into the feasibility of disposing alum sludge in raw wastewater. However, there are some issues, which were not completely addressed in this study and required further attention.

- This study is a bench scale study. However, a pilot scale study is required before implementing this alternative disposal option of the WTP alum sludge. A pilot plant study is important for determining the optimum mixing time and the amount of extra solid generated as a result of this disposal option. In addition, pilot plant study will provide a better understanding of the scale-up factor required for full scale application.
- The effect of pH and temperature on phosphorus adsorption was not very conclusive. The range of pH and temperature evaluated in this study was narrow and it was difficult to identify any specific trend in this range. Therefore, further work is required to determine the effect of pH and temperature on phosphorus removal considering a wide range of pH and temperature levels.
- To conduct the desorption test in duplicate more samples should be preserved earlier from the equilibrium test.
- Cost-benefit analysis must be performed in order to evaluate the feasibility of this alternative disposal option.

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APPENDIX A

Standard curve for orthophosphate concentration

Table A—1. Standard curve (A) calculation data

Orthophosphate (mg/l-P)	Abs read at 890 nm (1)	Abs read at 890 nm (2)	Mean abs read	Abs read after subtracting (blank + pillow)
Blank + pillow	0.004	0.003	0.004	
0	0	0	0	0
0.25	0.197	0.194	0.196	0.192
0.5	0.372	0.387	0.380	0.376
0.75	0.553	0.552	0.553	0.549
1	0.759	0.759	0.759	0.756
1.25	0.963	0.961	0.962	0.959

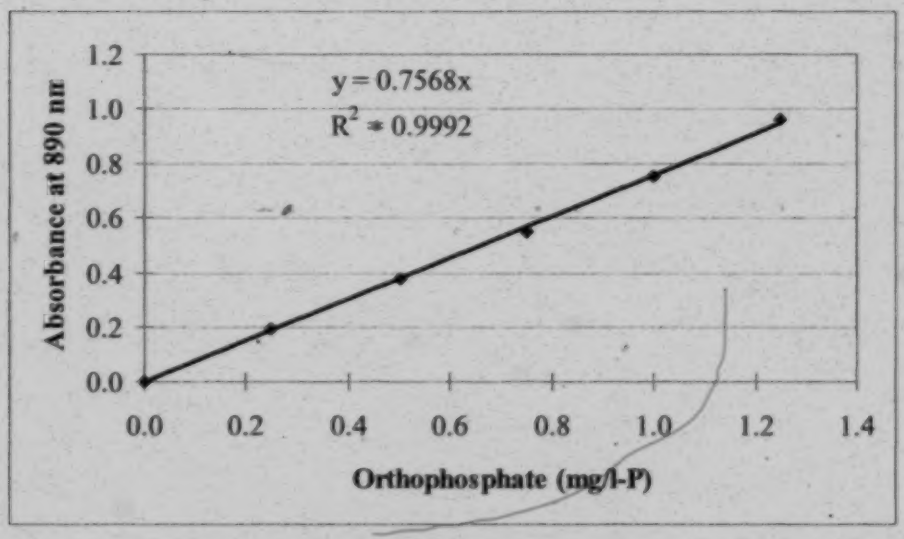

Figure A-1. Standard curve (A) developed for concentration 0 to 1.25 mg-P/l.

Table A-2 Standard curve (B) calculation data

Orthophosphate (mg/l-P)	Abs. read at 890 nm(1)	Abs. read at 890 nm(2)	Avg. abs. read	Abs read after subtracting (blank + pillow)
Blank + pillow	0.005	0.003	0.004	
0	0	0	0	0
0.25	0.166	0.165	0.1655	0.1615
0.5	0.361	0.363	0.362	0.358
0.75	0.56	0.562	0.561	0.557
1	0.734	0.74	0.737	0.733

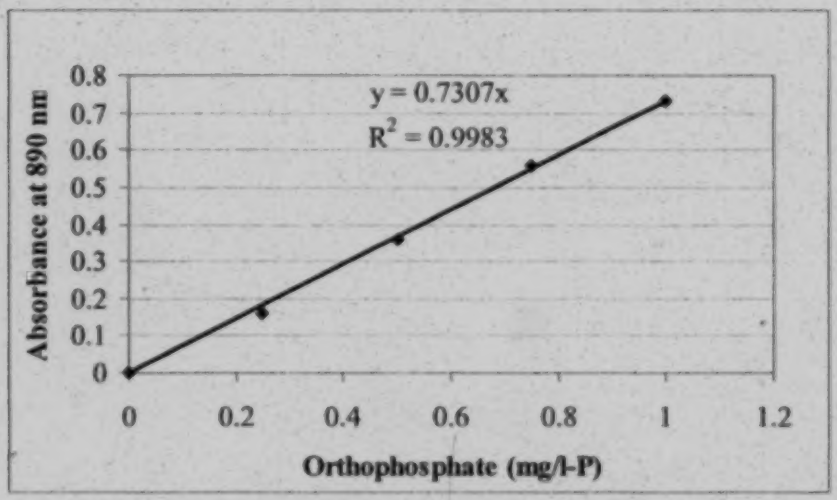

Figure A-2 Standard curve (B) developed for concentration 0 to 1 mg-P/l.

APPENDIX B

Alum sludge and raw sewage characteristics

Table B-1. Alum sludge pH.

Sampling date	Sample	pH	Mean pH
8-Aug	Alum Sludge (A)	7.30	
8-Aug	Alum Sludge (B)	7.25	7.26
8-Aug	Alum Sludge (C)	7.26	
23-Aug	Alum Sludge (A)	7.13	
23-Aug	Alum Sludge (B)	7.13	7.15
23-Aug	Alum Sludge (C)	7.19	
30-Aug	Alum Sludge (A)	7.22	7.20
30-Aug	Alum Sludge (B)	7.17	
6-Sep	Alum Sludge (A)	7.01	7.05
6-Sep	Alum Sludge (B)	7.09	

* A, B and C represent three replicates

Table B-2. Raw sewage pH.

Sampling date	Sample	pH	Mean pH
8-Aug	Raw sewage (A)	7.45	
8-Aug	Raw sewage (B)	7.50	7.49
8-Aug	Raw sewage (C)	7.53	
23-Aug	Raw sewage (A)	7.64	7.54
23-Aug	Raw sewage (B)	7.44	
30-Aug	Raw sewage (A)	7.59	
30-Aug	Raw sewage (B)	7.58	7.58
30-Aug	Raw sewage (C)	7.56	
6-Sep	Raw sewage (A)	7.71	
6-Sep	Raw sewage (B)	7.72	7.71
6-Sep	Raw sewage (C)	7.70	

* A, B and C represent three replicates

Table B-3. Alum sludge alkalinity.

Sampling date	Sample*	Alkalinity (mg/l as $CaCO_3$)	Mean alkalinity (mg/l as $CaCO_3$)
8-Aug	Alum Sludge (A)	135	
8-Aug	Alum Sludge (B)	110	128.8
8-Aug	Alum Sludge (C)	130	
8-Aug	Alum Sludge (C)	140	
30-Aug	Alum Sludge (A)	178.2	173.3
30-Aug	Alum Sludge (B)	168.3	
6-Sep	Alum Sludge (A)	137.2	125.0
6-Sep	Alum Sludge (B)	112.7	

* A, B and C represent three replicates

Table B-4. Raw sewage alkalinity.

Sampling date	Sample*	Alkalinity (mg/l as $CaCO_3$)	Mean alkalinity (mg/l as CaCO3)
8-Aug	Raw sewage (A)	345	
8-Aug	Raw sewage (B)	350	341.7
8-Aug	Raw sewage (C)	330	
30-Aug	Raw sewage (A)	391.1	
30-Aug	Raw sewage (B)	396	397.7
30-Aug	Raw sewage (C)	405.9	
6-Sep	Raw sewage (A)	441	
6-Sep	Raw sewage (B)	470.4	439.4
6-Sep	Raw sewage (C)	406.7	

* A, B and C represent three replicate

Table B-5. Alum sludge TS and TSS.

Sampling date	Sample*	TS (mg/l)	Mean TS (mg/l)	TSS (mg/l)	Mean TSS (mg/l)	% TSS in terms of TS
8-Aug	Alum Sludge (A)	5792	5411	1620	1855	34
8-Aug	Alum Sludge (B)	5030		2090		
23-Aug	Alum Sludge (A)	4934		4360		
23-Aug	Alum Sludge (B)	4676	4772.3	4240	4246.7	89
23-Aug	Alum Sludge (C)	4707		4140		
30-Aug	Alum Sludge (A)	23680		23600		
30-Aug	Alum Sludge (B)	23876	23808	23600	23266.7	98
30-Aug	Alum Sludge (C)	23868		22600		
6-Sep	Alum Sludge (A)	1746		1290		
6-Sep	Alum Sludge (B)	1628	1719.3	1390	1330	77
6-Sep	Alum Sludge (C)	1784		1310		

* A, B and C represent three replicates

Table B-6. Raw sewage TS and TSS.

Sampling date	Sample*	TS (mg/l)	Mean TS (mg/l)	TSS (mg/l)	Mean TSS (mg/l)
8-Aug	Raw sewage (A)	576	576	336	336
23-Aug	Raw sewage (A)	1101		188	
23-Aug	Raw sewage (B)	1087	1105.7	234	221.3
23-Aug	Raw sewage (C)	1129		242	
30-Aug	Raw sewage (A)	1125		152	
30-Aug	Raw sewage (B)	1176	1134.3	136	141.3
30-Aug	Raw sewage (C)	1102		136	
6-Sep	Raw sewage (A)	1003		166	
6-Sep	Raw sewage (B)	964	980.7	158	164.7
6-Sep	Raw sewage (C)	975		170	

* A, B and C represent three replicates

Table B-7. Alum sludge orthophosphate and total phosphorus concentration.

Sampling date	Sample*	Ortho-phosphate (mg/l-P)	Mean ortho-phosphate (mg/l-P)	Total P (mg/l-P)	Mean total P (mg/l-P)
8-Aug	Alum Sludge (A)	0.04		<.01	
8-Aug	Alum Sludge (B)	0.01	0.02	0.1	0.1
8-Aug	Alum Sludge (C)	0.02		<.01	
22-Aug	Alum Sludge (A)	0.00		1.7	
22-Aug	Alum Sludge (B)	0.00	0.00	1.7	1.7
22-Aug	Alum Sludge (C)	0.01		1.6	
30-Aug	Alum Sludge (A)	0.01		13.3	
30-Aug	Alum Sludge (B)	0.02	0.01	12.8	12.1
30-Aug	Alum Sludge (C)	0.01		10.3	
6-Sep	Alum Sludge (A)	0.04		0.7	
6-Sep	Alum Sludge (B)	0.04	0.04	ns	0.7
6-Sep	Alum Sludge (C)	0.03		ns	

* A, B and C represent three replicates

Table B-8. Raw sewage orthophosphate and total phosphorus concentration.

Sampling date	Sample*	Ortho-phosphate (mg/l-P)	Mean ortho-phosphate (mg/l-P)	Total P (mg/l-P)	Mean total P (mg/l-P)
8-Aug	Raw sewage (A)	5.2		9.7	
8-Aug	Raw sewage (B)	4.6	4.9		9.7
8-Aug	Raw sewage (C)	5.0			
23-Aug	Raw sewage (A)	7.2		11.1	
23-Aug	Raw sewage (B)	9.5	8.2	11.2	11.1
23-Aug	Raw sewage (C)	7.9		11	
30-Aug	Raw sewage (A)	6.3		9.9	
30-Aug	Raw sewage (B)	6.6	6.5	10	9.9
30-Aug	Raw sewage (C)	6.6		9.8	
6-Sep	Raw sewage (A)	8.7		15.1	
6-Sep	Raw sewage (B)	9.5	9.4	15.3	15.4
6-Sep	Raw sewage (C)	9.9		15.7	

* A, B and C represent three replicates.

Table B-9. Alum sludge total aluminum and dissolved aluminum concentration.

Sampling date	Sample*	Total Al (mg/l)	Mean total Al (mg/l)	Dissolved Al (mg/l)	Mean dissolved Al (mg/l)
8-Aug	Alum Sludge (A)	203	208.5	0.287	0.455
8-Aug	Alum Sludge (B)	214		0.622	
22-Aug	Alum Sludge (A)	348		0.318	
22-Aug	Alum Sludge (B)	351	350	0.294	0.299
22-Aug	Alum Sludge (C)	351		0.285	
30-Aug	Alum Sludge (A)	2240		0.289	
30-Aug	Alum Sludge (B)	2160	2183.3	0.288	0.291
30-Aug	Alum Sludge (C)	2150		0.297	
6-Sep	Alum Sludge (A)	184		0.256	
6-Sep	Alum Sludge (B)	184	183.7	0.256	0.257
6-Sep	Alum Sludge (C)	183		0.258	

* A, B and C represent three replicates

Table B-10. Raw sewage total aluminum and dissolved aluminum concentration.

Sampling date	Sample*	Total Al (mg/l)	Mean total Al (mg/l)	Dissolved Al (mg/l)	Mean dissolved Al (mg/l)
23-Aug	Raw sewage (A)	1.2		0.281	
23-Aug	Raw sewage (B)	1.32	1.31	0.283	0.287
23-Aug	Raw sewage (C)	1.41		0.297	
30-Aug	Raw sewage (A)	1.24		0.3	
30-Aug	Raw sewage (B)	1.06	1.14	0.295	0.298
30-Aug	Raw sewage (C)	1.12		0.275	
6-Sep	Raw sewage (A)	1.23		0.242	
6-Sep	Raw sewage (B)	1.24	1.23	0.244	0.242
6-Sep	Raw sewage (C)	1.22		0.241	

* A, B and C represent three replicates

Table B-11. Total aluminum in alum sludge as a percentage of total solids.

Sampling date	Sample*	TS (mg/l)	Mean TS (mg/l)	Al (mg/l)	Mean Al (mg/l)	% Al in TS
8-Aug	Alum Sludge (A)	5792	5411	203	208.5	3.9
8-Aug	Alum Sludge (B)	5030		214		
23-Aug	Alum Sludge (A)	4934		348		
23-Aug	Alum Sludge (B)	4676	4772.3	351	350	7.3
23-Aug	Alum Sludge (C)	4707		351		
30-Aug	Alum Sludge (A)	23680		2240		
30-Aug	Alum Sludge (B)	23876	23808	2160	2183.3	9.2
30-Aug	Alum Sludge (C)	23868		2150		
6-Sep	Alum Sludge (A)	1746		184		
6-Sep	Alum Sludge (B)	1628	1719.3	184	183.7	10.7
6-Sep	Alum Sludge (C)	1784		183		

* A, B and C represent three replicates

APPENDIX C

Temperature effects on phosphorus removal

Table C-1. Equilibrium orthophosphate and total P concentration in solution at 19°C (pH 7.5).

Test Date	Dilution ratio*	Orthophosphate (mg/l-P)	Mean orthophosphate (mg/l-P)	Total P (mg/l-P)	Mean total P (mg/l-P)
9-Aug	1:4(A)	0.17	0.16	0.90	
9-Aug	1:4 (B)	0.16		0.87	0.87
9-Aug	1:4(C)	0.15		0.84	
9-Aug	1:9(A)	0.73		1.5	
9-Aug	1:9(B)	0.67	0.71	1.45	1.49
9-Aug	1:9 (C)	0.74		1.52	
9-Aug	1:19(A)	1.94		2.72	
9-Aug	1:19(B)	1.83	1.86	2.65	2.64
9-Aug	1:19 (C)	1.81		2.56	
9-Aug	1:39(A)	2.80		3.7	
9-Aug	1:39(B)	2.73	2.82	3.6	3.66
9-Aug	1:39 (C)	2.94		3.68	
9-Aug	1:79(A)	3.61		4.25	
9-Aug	1:79(B)	3.47	3.43	4.51	4.44
9-Aug	1:79 (C)	3.21		4.56	

*Dilution ratio = volume sludge: volume raw sewage; A, B, and C represent replicates samples.

Table C-2. Orthophosphate adsorption from raw sewage per unit mass of total aluminum at 19°C (pH 7.5).

Total Al (mg)	Initial Orthophosphate (mg/l-P)	Equilibrium Orthophosphate (mg/l-P)	mg ortho-phosphate removed	% Ortho-phosphate removed	(mg PO_4^{3-}-P removed/g Al_T)
10.7	3.9	0.2	0.95	95.9	88.4
5.4	4.4	0.7	0.93	83.9	173.9
2.7	4.7	1.9	0.71	60.3	263.6
1.3	4.8	2.8	0.50	41.2	370.1
0.7	4.9	3.4	0.55	29.5	536.8

Table C-3. Total P adsorption from raw sewage at 19°C (pH 7.5).

Total Al (mg)	Initial total P (mg/l-P)	Equilibrium total P (mg/l-P)	mg total P removed	% total P removed	mg total P removed/ g Al_T
10.7	7.77	0.87	1.73	88.8	161.2
5.4	8.73	1.49	1.81	82.9	338.4
2.7	9.21	2.64	1.64	71.3	613.8
1.3	9.45	3.66	1.45	61.3	1082.3
0.7	9.57	4.44	2.06	53.6	1917.8

Table C-4. Equilibrium orthophosphate and total phosphorus concentration in solution at 12°C (pH 7.5).

Test Date	Dilution ratio*	Orthophosphate (mg/l-P)	Mean ortho-phosphate (mg/l-P)	Total P (mg/l-P)	Mean total P (mg/l-P)
31-Aug	1:19(A)	0.03	0.03	0.71	
31-Aug	1:19(B)	0.03		0.64	0.69
31-Aug	1:19 (C)	0.04		0.73	
31-Aug	1:39(A)	0.14	0.19	1.12	
31-Aug	1:39(B)	0.21		1.21	1.18
31-Aug	1:39 (C)	0.23		1.21	
31-Aug	1:79(A)	0.82	0.85	1.59	
31-Aug	1:79(B)	0.79		1.54	1.64
31-Aug	1:79 (C)	0.95		1.79	
31-Aug	1:159(A)	2.19	2.17	3.48	
31-Aug	1:159(B)	2.12		3.17	3.28
31-Aug	1:159 (C)	2.19		3.18	
31-Aug	1:319(A)	3.90	3.76	5.44	
31-Aug	1:319(B)	3.66		5.56	5.45
31-Aug	1:319 (C)	3.73		5.36	
31-Aug	1:399(A)	4.01		5.34	
31-Aug	1:399(B)	3.87	3.84	5.92	5.63
31-Aug	1:399 (C)	3.63		5.64	

*Dilution ratio = volume sludge: volume raw sewage; A, B, and C represent replicate samples.

Table C-5. Orthophosphate adsorption from raw sewage at 12°C (pH 7.5).

Total Al (mg)	Initial orthophosphate (mg/l-P)	Equilibrium orthophosphate (mg/l-P)	Ortho-phosphate removed (mg)	Ortho-phosphate removed (%)	mg PO_4^{3-}-P removed/g Al_T
27.3	6.16	0.03	1.53	99.5	56.11
13.6	6.32	0.19	1.53	96.9	112.22
6.8	6.40	0.85	1.11	86.7	203.24
3.4	6.44	2.17	0.85	66.4	313.20
1.7	6.46	3.76	0.67	41.7	395.99
1.4	6.47	3.79	0.67	41.4	491.07

Table C-6. Total P adsorption from raw sewage at 12°C (pH 7.5).

Total Al (mg)	Initial Total P (mg/l-P)	Equilibrium total P (mg/l-P)	Total P removed (mg)	Total P removed (%)	mg total P removed/g Al_T
27.3	10.00	0.69	2.33	93.1	85.27
13.6	9.95	1.18	2.19	88.1	160.58
6.8	9.92	1.64	1.66	83.9	303.30
3.4	9.90	3.28	1.33	66.9	485.65
1.7	9.90	5.45	1.11	44.9	652.32
1.4	9.90	5.64	1.07	43.1	780.55

Table C-7. Equilibrium orthophosphate and total phosphorus concentration in solution at 5°C (pH 7.5).

Test Date	Dilution ratio*	Orthophosphate (mg/l-P)	Mean orthophosphate (mg/l-P)	Total P (mg/l-P)	Mean total P (mg/l-P)
24-Aug	1:4(A)	0.12		0.53	
24-Aug	1:4(B)	0.10	0.10	0.42	0.43
24-Aug	1:4 (C)	0.10		0.34	
24-Aug	1:9(A)	0.62		0.66	
24-Aug	1:9(B)	0.33	0.52	0.71	0.69
24-Aug	1:9 (C)	0.62		0.69	

Test Date	Dilution ratio*	Orthophosphate (mg/l-P)	Mean orthophosphate (mg/l-P)	Total P (mg/l-P)	Mean total P (mg/l-P)
24-Aug	1:19(A)	0.96		1.08	
24-Aug	1:19(B)	0.89	0.95	1.16	1.10
24-Aug	1:1 (C)	1.00		1.07	
24-Aug	1:39(A)	2.68		2.57	
24-Aug	1:39(B)	3.07	2.64	2.98	2.69
24-Aug	1:39 (C)	2.16		2.53	
24-Aug	1:79(A)	3.55		3.53	
24-Aug	1:79(B)	2.99	3.11	3.65	3.61
24-Aug	1:79 (C)	2.79		3.66	

*Dilution ratio = volume sludge: volume raw sewage; A, B, and C represent replicates samples.

Table C-8. Orthophosphate adsorption from raw sewage per unit mass of total aluminum at 5°C (pH 7.5).

Total Al (mg)	Initial orthophosphate (mg/l-P)	Equilibrium orthophosphate (mg/l-P)	Ortho-phosphate removed (mg)	Ortho-phosphate removed (%)	mg PO_4^{3-}-P removed/g Al_T
17.5	6.6	0.1	1.6	98.4	92.23
8.8	7.4	0.5	1.7	92.9	195.95
4.4	7.8	1.0	1.7	87.8	390.87
2.2	8.0	2.6	1.3	67.0	612.45
1.1	8.1	3.1	1.3	61.6	1139.71

Table C-9. Total P adsorption from raw sewage per unit aluminum of alum sludge at 5°C (pH 7.5).

Total Al (mg)	Initial Total P (mg/l-P)	Equilibrium total P (mg/l-P)	Total P removed (mg)	Total P removed (%)	mg total P removed/g Al_T
17.5	9.22	0.43	2.20	95.3	125.55
8.75	10.16	0.69	2.37	93.2	270.70
4.375	10.63	1.10	2.38	89.7	544.38
2.2	10.87	2.69	2.04	75.3	933.90
1.1	10.98	3.61	1.84	67.1	1684.38

Table C-10. The isotherm parameters and the R^2 values for Langmuir and Freundlich isotherms for orthophosphate using solver.

Temperature	Langmuir isotherm, $q = \frac{q_m bC}{(1+bC)}$			Freundlich isotherm, $q = KC^{1/n}$		
	b	qm	R^2	1/n	K	R^2
19° C	0.02	9312.89	0.90	0.74	192.38	0.90
12° C	0.59	624.79	0.93	0.49	227.24	0.96
5° C	0.002	178516.88	0.88	0.90	348.56	0.88

Table C-11. The isotherm parameters and the R^2 values for Langmuir and Freundlich isotherms for total phosphorus using solver

Temperature	Langmuir isotherm, $q = \frac{q_m bC}{(1+bC)}$			Freundlich isotherm, $q = KC^{1/n}$		
	b	qm	R^2	1/n	K	R^2
19° C	0.0005	708270.39	0.84	2.06	85.42	0.97
12° C	0.06	2984.91	0.97	0.86	167.59	0.97
5° C	0.0008	562303.52	0.95	1.12	374.21	0.96

APPENDIX D

pH effects on phosphorus removal

Table D-1. pH effect on orthophosphate and total phosphorus removal from raw sewage.

Test Date	Sample*	Orthophosphate (mg/l-P)	Mean Orthophosphate (mg/l-P)	Total P (mg/l-P)	Mean total P(mg/l-P)
7-Sep	pH 6.5 (A)	6.2		7.1	
7-Sep	pH 6.5 (B)	5.6	5.8	7.0	7.0
7-Sep	pH 6.5 (C)	5.4		6.9	
7-Sep	pH 7(A)	5.9		6.7	
7-Sep	pH 7(B)	5.5	5.7	6.6	6.6
7-Sep	pH 7(C)	5.7		6.6	
7-Sep	pH 8(A)	5.4		6.4	
7-Sep	pH 8(B)	5.5	5.4	6.5	6.4
7-Sep	pH 8(C)	5.3		6.2	

*A, B and C represent replicate samples.

Table D-2. Effect of pH on orthophosphate adsorption.

pH	Total Al (mg)	Initial Orthophosphate (mg/l-P)*	Equilibrium Orthophosphate (mg/l-P)*	Orthophosphate removed (mg-P)	mg PO_4^{3-}-P removed/g Al_T
6.5	2.3	8.93	5.75	0.79	346
7	2.3	8.93	5.70	0.81	351
8	2.3	8.93	5.42	0.88	382

* Solution volume = 250 ml.

Table D-3. Effect of pH on total phosphorus adsorption.

pH	Total Al (mg)	Initial total P (mg/l-P)*	Equilibrium total P (mg/l-P)*	mg total P removed	mg total P removed/g Al
6.5	2.3	14.64	7.00	1.91	831.6
7	2.3	14.64	6.63	2.00	871.9
8	2.3	14.64	6.40	2.06	897.3

* Solution volume = 250 ml.

Hypothesis:

Null hypothesis: No difference in mean orthophosphate adsorption density values at three pH levels.

Alternate hypothesis: The mean orthophosphate adsorption density values are different at three pH levels.

Table D-4. Single factor ANOVA for mg orthophosphate removed/g Al_T at three pH levels.

SUMMARY						
Groups	Count	Sum	Average	Variance		
pH 6.5	3	1037.70	345.90	2016.62		
pH 7	3	1052.60	350.87	397.86		
pH 8	3	1145.49	381.83	115.73		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2274.54	2	1137.27	1.35	0.33	5.14
Within Groups	5060.43	6	843.41			
Total	7334.98	8				

* As F < Fcritical, accept the null hypothesis, no difference in mean at three pH levels, at 95% confidence limit.

Hypothesis:

Null hypothesis: No difference in mean total phosphorus adsorption density values at three pH levels.

Alternate hypothesis: The mean total phosphorus adsorption density values are different at three pH levels.

Table D-5. Single factor ANOVA for mg total phosphorus removed/g Al_T at three pH levels.

SUMMARY						
Groups	Count	Sum	Average	Variance		
pH 6.5	3	2494.68	831.56	99.60		
pH 7	3	2615.55	871.85	115.02		
pH 8	3	2691.78	897.26	276.68		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	6585.22	2	3292.61	20.11	0.002	5.14
Within Groups	982.61	6	163.77			
Total	7567.83	8				

* As F > Fcritical, reject the null hypothesis, difference in mean at three pH levels, at 95% confidence limit.

APPENDIX E

Desorption test of phosphorus

Table E-1. Orthophosphate released to solution at pH 5 and 9 (tests conducted at 19°C).

Test Date	Sample*	Total Al added (g)	Solution volume (ml)	PO_4^{3-} released to solution (mg/l-P)	mg PO_4^{3-}-P released/g Al_T
17-Oct	1:19(pH 5)	0.0079	200	0.05	1.3
17-Oct	1:19(pH 9)	0.0079	200	0.05	1.3
17-Oct	1:39(pH 5)	0.0054	200	0.12	4.4
17-Oct	1:39(pH 9)	0.0054	200	0.11	4.1
17-Oct	1:79(pH 5)	0.0044	200	0.43	19.5
17-Oct	1:79(pH 9)	0.0044	200	0.45	20.5

*Dilution ratio = volume sludge: volume raw sewage.

Table E-2. Orthophosphate removed from raw sewage using alum sludge (tests conducted at 5°C and pH 7.5).

Test Date	Dilution ratio*	Total Al added (g)	mg PO_4^{3-}-P removed	mg PO_4^{3-}-P removed/g Al_T
24-Aug	1:19	0.0044	1.71	390.87
24-Aug	1:39	0.0022	1.34	612.45
24-Aug	1:79	0.0009	1.00	1139.71

* Dilution ratio = volume sludge: volume raw sewage.

Table E-3. Total phosphorus released to solution at pH 5 and 9 (tests conducted at 19°C).

Test Date	Solution pH	Total Al (g)	Solution volume (ml)	Total P released to solution (mg/l-P)	mg total P released/g Al_T
17-Oct	5	0.0079	200	0.184	4.7
17-Oct	9	0.0079	200	0.212	5.4
17-Oct	5	0.0054	200	0.304	11.3
17-Oct	9	0.0054	200	0.287	10.6
17-Oct	5	0.0044	200	0.672	30.5
17-Oct	9	0.0044	200	0.655	29.8

Table E-4. Total phosphorus removed from raw sewage using alum sludge (tests conducted at 5°C and pH 7.5).

Test Date	Sample	Total Al added (g)	mg total P removed	mg total P removed/g Al_T
24-Aug	1:19(pH 7.5)	0.0044	2.38	544.38
24-Aug	1:39(pH 7.5)	0.0022	2.04	933.90
24-Aug	1:79(pH 7.5)	0.0009	1.47	1684.38

*Dilution ratio = volume sludge: volume raw sewage.

Table E-5. Two-way ANOVA without replicate for mg orthophosphate released/g Al_T at different pH levels

SUMMARY	Count	Sum	Average	Variance		
0.0079 g Al_T	2	2.63	1.31	0.00		
0.0054 g Al_T	2	8.62	4.31	0.07		
0.0044 g Al_T	2	39.84	19.92	0.37		
pH 5	3	25.25	8.42	94.51		
pH 9	3	25.83	8.61	105.33		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Total Al (g)	399.28	2	199.64	1022.67	0.001	19
pH	0.06	1	0.06	0.28	0.65	18.51
Error	0.39	2	0.20			
Total	399.72	5				

* As F < Fcritical, accept the null hypothesis, no difference in mean at two pH levels, at 95% confidence limit.

Table E-6. Two-way ANOVA without replicate for mg total phosphorus released/g Al_T at different pH levels.

SUMMARY	Count	Sum	Average	Variance		
0.0079 g Al_T	2	10.07	5.03	0.24		
0.0054 g Al_T	2	21.89	10.95	0.15		
0.0044 g Al_T	2	59.75	29.88	0.26		
pH 5	3	46.13	15.38	176.19		
pH 9	3	45.58	15.19	160.94		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Total Al (g)	673.67	2	336.83	1134.39	0.0009	19
pH	0.05	1	0.05	0.18	0.72	18.51
Error	0.59	2	0.30			
Total	674.32	5				

* As F<Fcritical, accept the null hypothesis, no difference in mean at two pH levels, at 95% confidence limit.

Appendix F

Review of analytical results

1.0 Introduction

This research project involves the evaluation of phosphorus removal from raw sewage using alum sludge. The method used to measure the orthophosphate concentration in this study is the PhosVer 3 (Ascorbic acid) method, which is based on HACH method. An important step of this method is to use phosVer 3 phosphate reagent pillow in a certain volume of sample as suggested by the manufacturer. This pillow reacts with the sample and indicates the presence of orthophosphate. HACH manufacturer has two types of pillows; catalogue no. 21060-69 and 2209-99. The former one suggests using one pillow for 10 ml sample, whereas the later suggests using 1 pillow for 5 ml. But all through the study, one pillow was used for every 10 ml sample.

So, the objective of the review of analytical methods is to evaluate the effect of higher volume of sample on orthophosphate concentration by comparing the respective standard curves.

2.0 Materials and methods

2.1 Materials

- Raw sewage, collected from Gold Bar wastewater treatment plant on Oct 17, 2005 and preserved in cold room.
- Phosphorus stock solution (50 mg/L-P), prepared on Oct. 19, 05.
- Known standards (0.25 mg/l-P, 0.50 mg/l-P, 0.75 mg/l-P and 1.00 mg/l-P) prepared on Oct. 20, 05.
- PhosVer3 phosphate reagent.

2.2 Methods

The method used for measuring orthophosphate concentration was the PhosVer 3 (Ascorbic acid) method, which was based on HACH method (Method 8048, Water analysis handbook, 1997).

2.2.1 The standard curve

Two standard curves were generated in this experiment using phosVer3 phosphate reagent pillows for two types (Catalogue no. 21060-69 and 2209-99). For the standard curve A prepared using pillows (applicable for 10 ml sample), the phosphorus concentration ranged from 0 to 1.25 mg/L and one phosVer3 phosphate reagent pillow was added in each 10 ml solution of known concentration as suggested by the manufacturer. For the standard curve B prepared using pillows (applicable for 5 ml sample), the range was 0 to 1 mg/l and one phosVer3 phosphate reagent pillow was added in each 10 ml solution of known concentration, although the volume suggested by the manufacturer in this case was 5 ml. The absorbance was measured at 890 nm using Ultrospec 2000 UV/Visible spectrophotometer. The absorbance verses concentration diagram for both curves was developed using linear regression analysis. Each sample was analyzed in duplicate. Detailed calculation is provided in Appendix A.

2.2.2 Method of known addition

Sometimes standard curve may require standards that closely match the composition of the sample. Because, due to matrix effect, the standard curve generated for simple sample, might not be applicable for complex samples (APHA, 1997). This procedure, known as method of standard addition was also evaluated here in order to justify the acceptability of the new standard curve. For this purpose, known amount of phosphorus (1 mg/l-P) was added in certain volume of raw sewage. Then, both the raw sewage sample with known addition and the raw sewage alone were analyzed for measuring the phosphorus content using the standard curve developed earlier (for the pillows applicable for 5 ml sample). The difference between the spiked and unspiked sample should be equal to the amount of phosphorus added in the raw sewage. To add 1 mg/l – P in raw sewage, 1 ml phosphorus stock solution (50 mg/l) was added with 49 ml of raw sewage and mixed properly. Then the absorbance for both the sample with known addition and raw sewage were measured at 890 nm using Ultrospec 2000 spectrophotometer. The test was performed in triplicate and each sample was analyzed in duplicate.

3.0 Results and discussion

3.1 Standard curve

The standard curve A developed with pillows (applicable for 10 ml) is shown in Figure 3-1 and the curve B developed for the pillow (applicable for 5 ml sample) is shown in Figure 3-2. The former curve showed linear fit within phosphorus concentration 0 – 1.25 mg/l-P, whereas the later curve showed linear fit within phosphorus concentration 0 – 1 mg/l-P. The R^2 values for the former curve and the later curve were 0.9992 and 0.9983 respectively. This indicates that both curves fit well with the data points.

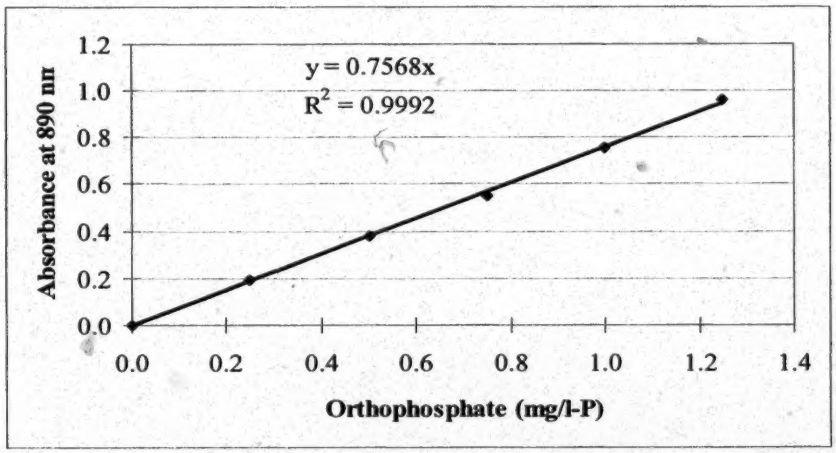

Figure 3-1 Standard curve (A) developed with pillow (for 10 ml sample)

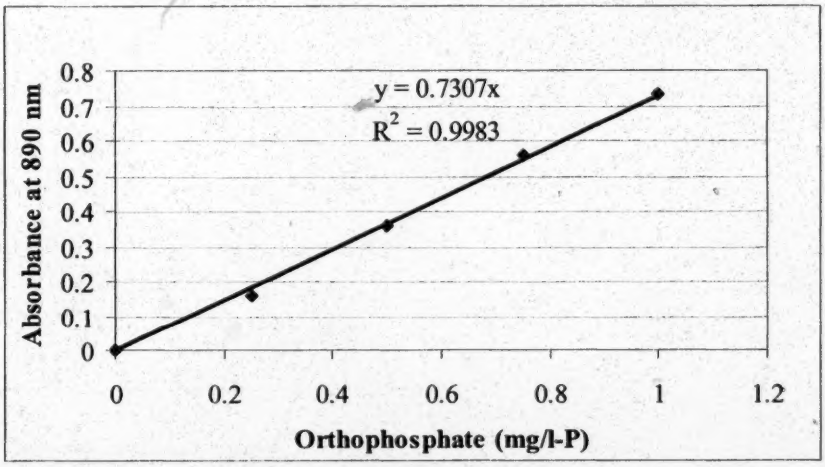

Figure 3-2 Standard curve (B) developed with pillow (for 5 ml sample)

3.2 The effect on previous results

The following tables, Table 3-1 to Table 3-3 show the comparison of phosphorus concentration determined by the standard curve A generated for phosVer 3 phosphate reagent pillow (for 10 ml sample) and the standard curve B generated for the pillows (for 5 ml sample) for the runs where the later pillows were used.

Use of higher volume then the suggested one has some effects on the previous runs phosphorus concentration results. While conducting the 5°C run, 12°C run and pH effect run each pillow was used for 10 ml sample although according to manufacturer's suggestion the sample volume should be 5 ml. After building the new standard curve (B) (each pillow used for 10 ml sample), it was tried to use the absorbance data to shift the concentration accordingly. In the Table 3-1, 3-2 and 3-3 the phosphorus concentration of the previous run results and the modified results are shown. This indicates that the phosphorus concentration measured earlier was relatively less then the modified one. With the use of new standard curve these absorbance now give the higher concentration.

Table 3-1. Temperature effect on phosphorus concentration at 5° C.

Sample*	Abs. at 890 nm (1)	Abs. at 890 nm (2)	Mean abs. read	Concentration determined by standard curve A (mg/l-P)	Concentration determined by standard curve B (mg/l-P)
1:4(A)	0.126	0.127	0.127	0.116	0.120
1:4(B)	0.111	0.106	0.109	0.092	0.095
1:4 (C)	0.112	0.109	0.111	0.094	0.098
1:9(A)	0.503	0.498	0.501	0.598	0.619
1:9(B)	0.287	0.285	0.286	0.314	0.326
1:9 (C)	0.501	0.502	0.502	0.599	0.621
1:19(A)	0.366	0.37	0.368	0.461	0.478
1:19(B)	0.343	0.346	0.345	0.430	0.445
1:1 (C)	0.385	0.386	0.386	0.484	0.502
1:39(A)	0.607	0.605	0.606	0.776	0.803

Sample*	Abs. at 890 nm (1)	Abs. at 890 nm (2)	Mean abs. read	Concentration determined by standard curve A (mg/l-P)	Concentration determined by standard curve B (mg/l-P)
1:39(B)	0.693	0.692	0.693	0.890	0.922
1:39 (C)	0.493	0.491	0.492	0.625	0.647
1:79(A)	0.279	0.278	0.279	0.343	0.355
1:79(B)	0.237	0.238	0.238	0.289	0.299
1:79 (C)	0.226	0.22	0.223	0.270	0.279
Raw sewage (A)	0.54	0.54	0.540	0.692	0.717
Raw sewage (B)	0.711	0.71	0.711	0.918	0.950
Raw sewage (C)	0.595	0.595	0.595	0.765	0.792

*Dilution ratio = volume sludge: volume raw sewage; A, B, and C represent replicates samples.

Table 3-2. Temperature effect on phosphorus concentration at 12° C.

Sample*	Abs. at 890 nm (1)	Abs. at 890 nm (2)	Mean abs read	Concentration determined by standard curve A (mg/l-P)	Concentration determined by standard curve B (mg/l-P)
1:19(A)	0.08	0.08	0.080	0.031	0.032
1:19(B)	0.077	0.08	0.079	0.029	0.030
1:19 (C)	0.082	0.086	0.084	0.036	0.038
1:39(A)	0.066	0.069	0.068	0.068	0.070
1:39(B)	0.093	0.094	0.094	0.102	0.106
1:39 (C)	0.1	0.101	0.101	0.112	0.116
1:79(A)	0.196	0.197	0.197	0.239	0.247
1:79(B)	0.188	0.189	0.189	0.228	0.236
1:79 (C)	0.226	0.224	0.225	0.276	0.286
1:159(A)	0.339	0.334	0.337	0.423	0.439
1:159(B)	0.326	0.327	0.327	0.410	0.425
1:159 (C)	0.337	0.334	0.336	0.422	0.437
1:319(A)	0.587	0.586	0.587	0.754	0.781
1:319(B)	0.553	0.55	0.552	0.708	0.733
1:319 (C)	0.561	0.56	0.561	0.719	0.745
1:399(A)	0.31	0.308	0.309	0.387	0.401

Sample*	Abs. at 890 nm (1)	Abs. at 890 nm (2)	Mean abs read	Concentration determined by standard curve A (mg/l-P)	Concentration determined by standard curve B (mg/l-P)
1:399(B)	0.301	0.296	0.299	0.373	0.387
1:399 (C)	0.282	0.281	0.282	0.351	0.363
Raw sewage (A)	0.474	0.472	0.473	0.604	0.625
Raw sewage (B)	0.497	0.499	0.498	0.637	0.660
Raw sewage (C)	0.499	0.497	0.498	0.637	0.660

*Dilution ratio = volume sludge: volume raw sewage; A, B, and C represent replicates samples.

Table 3-3. pH effect on phosphorus concentration.

Sample	Abs. at 890 nm (1)	Abs. at 890 nm (2)	Mean abs. read	Concentration determined by standard curve A (mg/l-P)	Concentration determined by standard curve B (mg/l-P)
pH 5(A)	0.49	0.509	0.500	0.651	0.674
pH 5(B)	0.515	0.533	0.524	0.683	0.708
pH 5 (C)	0.515	0.518	0.517	0.673	0.697
pH 6.5 (A)	0.688	0.688	0.688	0.900	0.932
pH 6.5 (B)	0.623	0.621	0.622	0.813	0.842
pH 6.5 (C)	0.599	0.604	0.602	0.786	0.814
pH 7(A)	0.653	0.655	0.654	0.855	0.885
pH 7(B)	0.611	0.618	0.615	0.803	0.831
pH 7(C)	0.629	0.627	0.628	0.821	0.850
pH 8(A)	0.600	0.599	0.600	0.783	0.811
pH 8(B)	0.613	0.612	0.613	0.800	0.829
pH 8(C)	0.59	0.592	0.591	0.772	0.799
pH 9(A)	0.229	0.231	0.230	0.295	0.305
pH 9(B)	0.268	0.266	0.267	0.344	0.356
pH 9(C)	0.221	0.218	0.220	0.281	0.291
Raw sewage (A)	0.640	0.650	0.645	0.843	0.873
Raw sewage (B)	0.695	0.712	0.704	0.920	0.953
Raw sewage (C)	0.749	0.715	0.732	0.958	0.992

*Dilution ratio = volume sludge: volume raw sewage; A, B, and C represent replicates samples.

The new standard curve B (developed using pillows for 5 ml sample) has a concentration range between 0 to 1 mg/l –P. Any absorbance value which results in concentration value higher then 1 mg/l-P is not acceptable when this curve is used. From Table 3-1, it can be seen that all the phosphorus concentrations are less then 1 mg/l, which indicates that the use of this standard curve is valid.

3.3 Standard (0.6 mg/l-P) to check two methods

To check the accuracy of this new standard curve (B) one standard was made of .6 mg/l – P. By using new standard curve the concentration was found 0.595 mg/l-P which gives the recovery of 99.16%. The percent error was 5%, which was within the acceptable range of 5%.

3.4 Method of known addition

After the analysis the average difference in concentration between spiked and unspiked sample was found 1.03 mg/l-P, which was close to the known addition 1 mg/l-P. The average percent error was 4.53, which was within the range of acceptable limit for experimental and methodological error (5%). This indicates that this standard curve can be used for the determination of phosphorus in raw sewage. The detail calculation is shown in Appendix B.

4.0 Conclusion and recommendations

The main purpose of this review of analytical method is to compare the standard curves generated using different types of pillows and to justify the acceptability of the standard curves. According to HACH manufacturer, each pillow from catalogue no. 21060-69 can be used for 10 ml sample and each pillow from catalogue no. 2209-99 can be used for 5 ml sample. Although the 2nd type of pillow was suggested for 5 ml sample but all through the experiment, one pillow was used for each 10 ml sample. The results suggested that both the curves are pretty close for the concentration range 0 to 1 mg/l-P. As the phosphorus concentration in all the runs where the standard curve B was used was below

1 mg/l, use of this curve is acceptable. Form the method of known addition; it was found that the percent error while using the standard curve B was within the acceptable limit of ±5%. This suggests that this standard curve in not largely affected by the difference in sample.

Although the new standard curve seems to be able to compensate the data variation made in this research earlier but it is always preferable to use the right volume for phosVer3 phosphate reagent pillow suggested by the manufacturer.

REFERENCE

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HACH, 1997. Water Analysis Handbook, 3rd Edition. HACH Company, Loveland, Colorado, USA.

Appendix A

Standard curve

Table A-1. Standard curve A calculation data.

Date	Standard Concentration (mg/l-P)	Abs. read at 890 nm(1)	Abs. read at 890 nm(1)	Avg. abs. read	Abs. Read. after subtracting (blank + pillow)
5-Aug	Blank + pillow	0.004	0.003	0.004	
5-Aug	0	0	0	0	0
5-Aug	0.25	0.197	0.194	0.196	0.192
5-Aug	0.5	0.372	0.387	0.380	0.376
5-Aug	0.75	0.553	0.552	0.553	0.549
5-Aug	1	0.759	0.759	0.759	0.756
5-Aug	1.25	0.963	0.961	0.962	0.959

Table A-2. Standard curve B calculation data.

Date	Standard Concentration (mg/l-P)	Abs. read at 890 nm(1)	Abs. read at 890 nm(1)	Avg. abs. read	Abs. Read. after subtracting (blank + pillow)
20-Oct	Blank + pillow	0.005	0.003	0.004	
20-Oct	0	0	0	0	0
20-Oct	0.25	0.166	0.165	0.166	0.162
20-Oct	0.5	0.361	0.363	0.362	0.358
20-Oct	0.75	0.56	0.562	0.561	0.557
20-Oct	1	0.734	0.74	0.737	0.733

Standard (0.6 mg/l-P) to check

Table A-3. Calculations to check the standard (0.6 mg/l-P).

Sample	Sample volume	Abs. read at 890 nm(1)	Abs. read at 890 nm(2)	Avg. abs. read	Concentration (mg/l-P)
0.6 mg/L-P standard sol^n	10	0.439	0.438	0.4385	0.594
0.6 mg/L-P standard sol^n	5	0.452	-	0.452	0.592

APPENDIX B

Method of standard (1 mg/l-P) addition

Table B-1. Calculation of standard addition.

Date	Sample*	DF	Abs. read at 890 nm(1)	Abs. read at 890 nm(2)	Mean abs. read	Concentration (mg/l-P)
26-Oct	Blank + pillow		0.004	0.007	0.006	
26-Oct	RS (blank)	0.1	0.003	0.005	0.004	
26-Oct	RS (1)	0.1	0.491	0.499	0.495	6.644
26-Oct	RS (2)	0.1	0.491	0.488	0.490	6.569
26-Oct	RS (3)	0.1	0.494	0.493	0.494	6.624
26-Oct	RS+P (Blank)	0.1	0.007	0.008	0.008	
26-Oct	RS+P (1)	0.1	0.569	0.571	0.570	7.623
26-Oct	RS+P (2)	0.1	0.573	0.572	0.573	7.657
26-Oct	RS+P (3)	0.1	0.574	0.57	0.572	7.650

* RS indicates raw sewage and P indicates phosphorus and 1,2 and 3 are the triplicates.

The average raw sewage concentration = 6.612 mg/l-P

The average raw sewage and the known standard addition = 7.643 mg/l-P

So, the standard concentration = 1.03 mg/l-P

Average error (%) = (2.14+8.8+2.64)/3 = 4.52